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CHEMICAL REACTIONS OF METAL-METAL BONDED COMPOUNDS

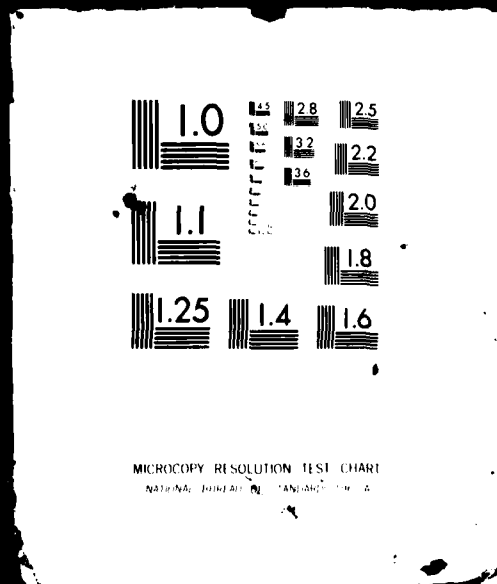OF THE TRANSITION ELEMENTS.

by

Malcolm H. Chisholm and Ian P. Rothwell

Prepared for Publication

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An overview of the reactivity patterns associated with compounds containing metal-to-metal bonds is presented. These reactions include formation, cleavage, photolysis, homolysis, oxidative-addition, reductive-elimination, substitution and catalytic sequences.

For Progress in Inorganic Chemistry

S. J. Lippard, Editor

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CHEMICAL REACTIONS OF METAL-METAL BONDED COMPOUNDS

OF THE TRANSITION ELEMENTS

by

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1. INTRODUCTION

1.1. Forward

The development of modern inorganic coordination chemistry, not unlike life, evolved from aqueous media. During the first half of this century, the principles associated with Werner coordination complexes, namely those containing a central metal cation surrounded by a group of neutral donor molecules or anions (e.g. H_2O, NH_3, Cl^-, CN^-, etc.), were delineated. However, the last 15 years (1) has seen the arrival of a new wave of coordination compounds in which a group of ligands surround two or more metal atoms that are directly bonded to each other. While perhaps even the majority of these compounds owe their existence to the use of non-aqueous solvents and anaerobic conditions, there are many that are readily synthesized in, and quite stable to water and our otherwise non-innocent atmosphere. At this time, virtually all the transition elements are known to form homo- or hetero-dinuclear compounds with metal-to-metal bonds which may be of integral (1, 2, 3 or 4) or fractional ($\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$ or $3\frac{1}{2}$) order. There are also large classes of cluster compounds, ranging from polynuclear metal carbonyls and other organometallics to polynuclear metal halides, oxides and chalconides, that contain delocalized metal-metal bonds. Initially, most of the interest in these compounds centered on ellucidations of structure, bonding and spectroscopic properties. More recently, there has been a growing interest in the reactivity patterns associated with these compounds (2). This article presents a survey of the types of reactions which have presently been established. The survey is not intended to be comprehensive, but rather to be illustrative of the

trends that are emerging in this new field. With time, perspectives, emphasis and fashionable opinions may change, but there is no doubt that the development of chemistry surrounding metal-to-metal bonds will be one of the most significant aspects of the post-Wernerian age of coordination chemistry.

1.2. Classification of Compounds

It is tempting to divide compounds containing metal-to-metal bonds into two classes. One group would include those compounds with metal atoms in formal oxidation states of zero or close to it. The majority of these compounds are polynuclear metal carbonyl compounds or organometallic species (3,4). Typically, the metal atoms attain an 18 valence shell of electrons as a result of forming metal-metal bonds. The metal-metal bonds are often single, their distances are long and the bonds appear weak, at least as judged by their kinetic lability toward cleavage reactions. The other group would comprise compounds with metal atoms in the middle range of their oxidation states with ligands that might be considered inorganic or classical in nature (e.g. halide, carboxylate, etc.) (5). This division, which is based on a ligand classification, separates areas of research interest. It separates "organometallic" chemistry from "coordination" chemistry, but has little relevance to the reactivity patterns of the metal-metal bonds. It is more instructive to consider reactivity within the context of the electronic structure of the metal-metal bonds and to classify compounds first by the number of metal atoms that are bonded to each other, and second according to specific molecular orbital configurations. Since at this time there has been no systematic, comprehensive study

of the reactivity of metal—metal bonded complexes, the findings lie rather like an incompleted jig-saw puzzle. The way in which the pieces fit together and are related to the electronic framework of the metal atoms is still a matter of opinion. It is therefore quite likely that in certain cases we have inappropriately or mistakenly grouped certain reactions together. Hopefully, our perspective of the order of things will serve as a stimulus for further thought and experiment.

A brief survey of the types of compounds to be considered and the electronic structure of the metal—metal bonds is required prior to discussion of reactivity.

1.2.1. Dinuclear Compounds

For dinuclear transition metal complexes, the metal—metal bonds arise primarily from the interactions of metal atomic d orbitals which are not used in metal ligand bonding. The assignment of M—M bond order rests on a large number of factors, including the number of electrons available for M—M bonding, the symmetry of the molecule, spectroscopic data and magnetic data, metal—to—metal distances and molecular conformations, and above all, internal consistency of all the data.

Interesting analogies can be drawn between the bonding in the diatomic molecules of the first short period and the homodinuclear molecules and coordination compounds of the transition elements. N_2 has a triple bond with a valence molecular orbital configuration $\sigma^2\pi^4$, whereas both C_2 and O_2 have double bonds of configuration $\pi^4\sigma^0$ and $\sigma^2\pi^4\pi^{*2}$, respectively. The orbital degeneracy of the π molecular orbitals, resulting from atomic p_x-p_x and p_y-p_y interactions, leads to a triplet ground state for O_2. The heterodia-

tomic molecule, NO, has a bond order of 2.5, resulting from the valence molecular orbital ground state configuration $\sigma^2\pi^4\pi^{*1}$. The ions NO^+ and NO^- have, respectively, triple and double bonds and are isoelectronic with N_2 and O_2. Correlations of bond order with bond lengths, bond dissociation energies, stretching force constants and frequencies can be made. These triumphs of molecular orbital theory now appear in virtually every freshman level chemistry text and it surely will not be long before the bonding schemes for certain dinuclear transition metal complexes are also included. The diatomic molecule, Mo_2, has a sextuple bond with a valence molecular orbital configuration $\sigma^2\pi^4\delta^4\sigma^2(6)$. There are hundreds of compounds with metal-metal quadruple bonds, $\sigma^2\pi^4\delta^2$ and triple bonds with configurations $\sigma^2\pi^4$ or $\sigma^2\pi^4\delta^2\delta^{*2}$ (7,8). The octet and EAN rule demand that F_2 and $Mn_2(CO)_{10}$ have element-element single bonds. On a molecular orbital basis, these are $\sigma^2\pi^4\pi^{*4}$ and $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$, respectively.

In Table 1.1, representative examples of dinuclear transition metal complexes are given, along with M-M bond order and the molecular orbital configuration. Several fine reviews and articles dealing with the theory and electronic structure of these types of compounds have recently been published and further discussion of these aspects is limited to the following.

1. For a given oxidation state +x, the effective nuclear charge exerted on the valence shell electrons decreases down a group. First row transition metal ions in their middle oxidation states rarely form strong metal-metal bonds. This is apparent in the chemistry of the Group 6 transition elements where, for oxidation number +3, molybdenum

Table 1.1. Some Examples of Dinuclear Transition Metal Complexes with Various Types of M-M Bond Order.

Compounds	Bond Order	Bonding Configuration
Mo_2	6	$\sigma^2\pi^4\delta^4\sigma^2$
$Mo_2(O_2CR)_4$, $Mo_2Cl_8^{4-}$, $W_2Cl_4(PR_3)_4$, $Re_2Cl_8^{2-}$	4	$\sigma^2\pi^4\delta^2$
$Mo_2(SO_4)_4^{3-}$, $MoW(O_2CBu^t)_4I$	3.5	$\sigma^2\pi^4\delta^1$
M_2X_6 (M = Mo, W; X = R, OR, NR_2)	3	$\sigma^2\pi^4$
$Cp_2Mo_2(CO)_4$	3	EAN Rule
$Re_2Cl_4(PR_3)_4$, $Os(2\text{-oxopyridine})_4Cl_2$, $Mo_2(F_2NCH_2PF_2)_4Cl_2$	3	$\sigma^2\pi^4\delta^2\delta*^2$
$Ru_2(O_2CR)_4Cl$	2.5	$\sigma^2\pi^4\delta^2\pi*^2\delta*^1$
$Mo_2(OPr^i)_8$, $W_2(OEt)_4Cl_4(HOEt)_2$	2	$\sigma^2\pi^2$
$Cp_2Co_2(CO)_2$	2	EAN Rule
$Cp_2Co_2(CO)_2^{\bar{}}$	1.5	EAN Rule
$Mo_2(OPr^i)_6X_4$ (X = Cl, Br, I)	1	σ^2
$Mn_2(CO)_{10}$, $Cp_2M_2(CO)_6$ (M = Cr, Mo, W)	1	EAN Rule

and tungsten form innumerable compounds with a central $(M{\equiv}M)^{6+}$ unit, but not one chromium analog is known (9).

2. Formation of M–M bonds is greatly dependent on the nature of the ligands (10,11). Two examples are well illustrative of this. (a) Mo_2Cl_{10} and $Mo_2Cl_4(OPr^i)_6$ are d^1–d^1 dimers with a common edge-shared octahedral geometry. From considerations of magnetism, structure and chemical reactivity, it has been shown that there is no M–M bond in the former and a single order M–M bond in the latter (12,13,14). (b) Compounds of formula M_2L_{10} (d^4–d^4) may exist as unbridged quadruply bonded compounds, e.g. $Re_2Cl_8L_2^{2-}$ (7,15), bridged doubly bonded compounds, e.g. $V_2(CO)_8(\mu-PR_2)_2$ (16,17) and metal-metal non-bonded, high spin, bridged compounds, e.g. $Re_2Cl_4(dppe)_2(\mu-Cl)_2$ (18,19). These have recently been scrutinized by Hoffmann and his coworkers (20).

3. Though atomic p orbital participation in M–M bonding in early transition metal dinuclear compounds appears of minimal significance, for the later elements d–p mixing becomes important. The tendency of d^8 Rh square planar cations to dimerize, e.g. $2Rh(CNR)_4^+ \rightarrow Rh_2(CNR)_8^{2+}$, (21,22), is quite contrary to chemical intuition. The stabilization of the dimer by d–p mixing can be understood in terms of the schematic molecular orbital energy level diagram shown in Figure 1.1.

1.2.2. Trinuclear Compounds

Linear, angular and triangular complexes are known and the latter may be equilatoral, with M–M bonds of multiple, single or fractional order, or isoscelese with the unique side having a different M–M bond order. The metal atoms may be bridged or unbridged by ligand atoms

Figure 1.1.   Schematic molecular orbital diagram showing how d_z2-p_z
mixing can stabilize the $Rh_2L_8^{2+}$ cation relative to the mononuclear
cation RhL_4^+.
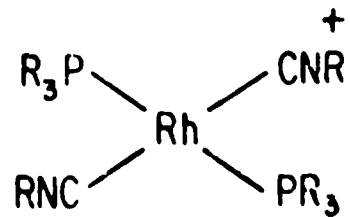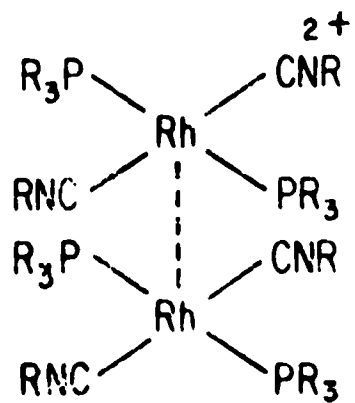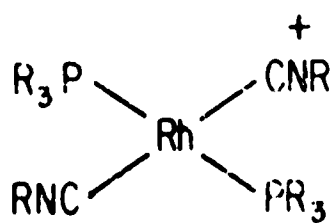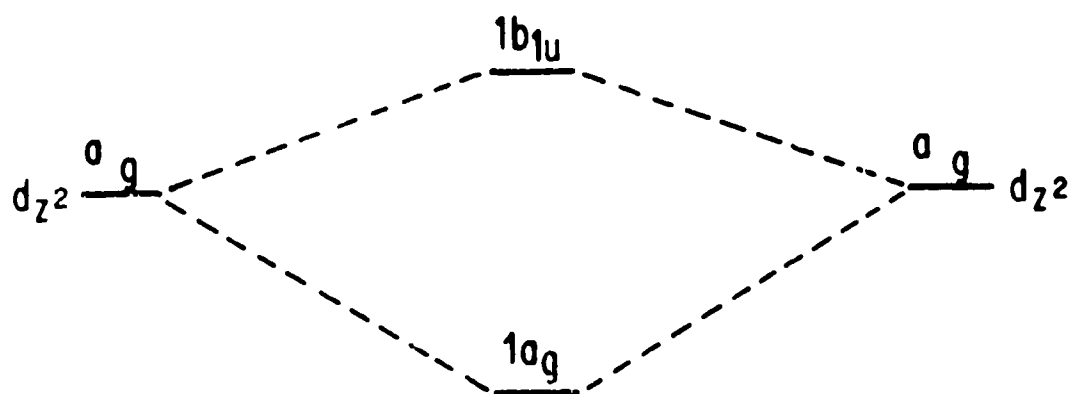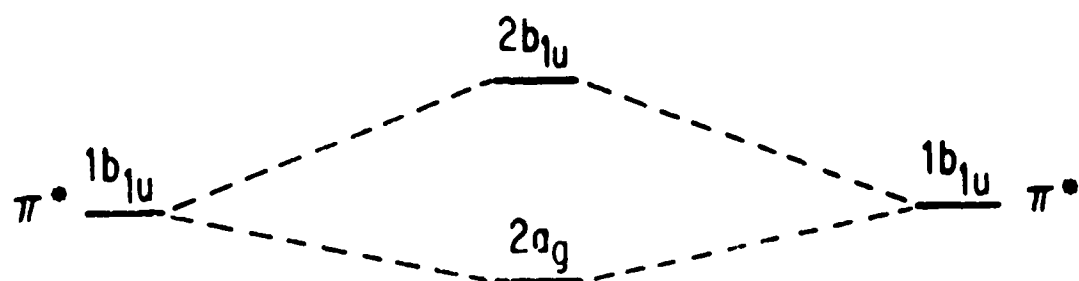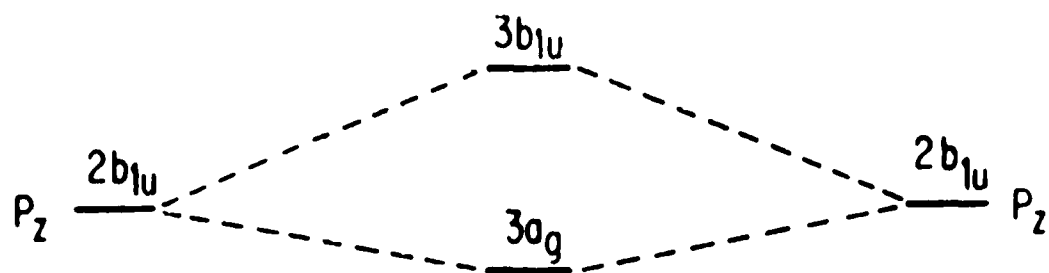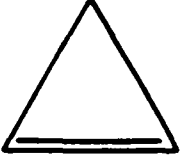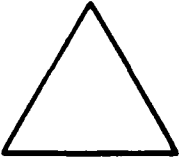
and the triangular group of metal atoms may be once or twice capped by triply bridging ligand atoms. In some instances, the metal–metal bonding may be satisfactorily accounted for by compliance to the EAN rule and valence bond theory. However, in most instances, a molecular orbital description based on symmetry considerations provides a rationale and understanding of bonding and electronic structure. This approach was first successfully applied by Cotton and Haas (23) to Re_3Cl_9. This molecule has D_{3h} symmetry and 12 electrons occupy molecular orbitals which are metal–metal bonding: $(a'_1)^2(a''_1)^2(e')^4(e'')^4$. In a valence bond description, this is equivalent to three Re–Re double bonds. Representative examples of trinuclear metal complexes are given in Table 1.2.

1.2.3. Tetra-, Penta-, Hexa- and Other Polynuclear Complexes

With increasing nuclearity, the possible geometrical arrangements increase rapidly. Four metal atoms may form a tetrahedron or a bisphenoid with D_{2d} geometry. The latter may be viewed as a distorted tetrahedron with four long and two short M–M distances. Alternatively, the tetrahedron can be "opened up" to form a butterfly or planar structure. These and other structures are all known. For five and six metal atom containing species, the geometric possibilities are increased, but less often realized, since the tendency to "cluster" favors the closed structures of the trigonal bipyramid and octahedron. The structures of many polynuclear metal carbonyl species can be predicted, or at least rationalized by a consideration of the types of orbitals and the number of electrons that are available for cluster bonding. These considerations form the basis for Wade's rule (24,25,26). Closo

Table 1.2.   Some Examples of Trinuclear Metal Complexes with their Valence Bond M-M Representations.

Compound	M-M Bonding
Re_3Cl_9	(double-line triangle)
$Os_3(CO)_{10}(\mu-H)_2$	(triangle with doubled base line)
$M_3(CO)_{12}$ (M = Fe, Ru, Os) $Mo_3S_4(CN)_9^{5-}$ $W_3(\mu_3-O)_2(\mu_2-O_2CR)_6(H_2O)_3^{2+}$	(triangle)
$Os_3(CO)_{10}X_2$ (X = Cl, OMe) $Pt_3(\mu_2-PPh_2)_3(PPh_3)_2(Ph)$	(open angle / two sides of triangle)
$Fe(CO)_4(AuL)_2$ $Os_3(CO)_{12}(CH_3)(H)$	(single line)

structures are favored when there are n + 1 electron pairs available for cluster bonding. When there are more than n + 1 electron pairs, the M_n cluster will open up to a nido or arachno structure. The analogy with the structures of boranes is apparent in this theory.

The octahedral grouping of metal atoms is seen in the very different (from carbonyl) compounds containing $M_6Cl_{12}^{2+}$ (M = Nb, Ta) and $M_6Cl_8^{4+}$ (M = W, Mo) (29) cores. These have, respectively, 16 and 24 electrons available for M–M bonding. The symmetry is such that all the electrons may be accommodated in M–M bonding molecular orbitals: $(a_{1g})^2-(a_{2u})^2(t_{1g})^6(t_{2g})^6$ for M = Nb and Ta and $(a_{1g})^2(t_{1u})^6(e_g)^4((t_{2g})^6(t_{2u})^6$ for M = Mo and W, corresponding to M–M bond orders of 2/3 and 1, respectively (5,23).

In certain high nuclearity carbonyl clusters, the arrangement of metal atoms has been found to resemble that of a section of a metallic structure. For example, the arrangement of metal atoms in $[Rh_{13}(CO)_{24}-H_x]^{x-}$, where x = 2 or 3 (30) and in $[Rh_{14}(CO)_{25}]^{4-}$ (31), represent the smallest possible units of hexagonal closest packed and body–centered cubic structures, respectively.

Rather interestingly, lower valent transition metal halide and oxide structures often contain repeating units which resemble those found in discrete dinuclear or cluster compounds. For example, in one form of MoO_2, which has a distorted rutile structure, the molybdenum atoms occur in pairs within the oxide lattice (32). The Mo–Mo distance is 2.511(1) Å, typical of the Mo≡Mo distances found in the dinuclear compounds $Mo_2(OPr^i)_8$ (33) and $Mo_2(OBu^t)_6(\mu-CO)$ (34). In the mixed metal oxides, $M_2Mo_3O_8$, where M = Mg, Mn(II), Fe(II), Co(II), Ni(II), Zn and Cd (36),

there are triangular Mo_3 units having six electrons in M–M bonding molecular orbitals as are found in many discrete coordination compounds (37). In $Ba_{1.13}Mo_8O_{16}$, there are chains of Mo_4O_{16} fused octahedra having either 10 or 12 cluster bonding electrons (38), while in $W_4(OEt)_{16}$, which has the same basic M_4O_{16} unit, there are eight electrons in M_4 cluster bonding molecular orbitals (39).

The scope of metal–metal bonding is thus immense, embracing the chemistry of metals, metal–surfaces, discrete dinuclear and cluster compounds and polymeric metal–oxides, –halides and –chalconides. Our present limited understanding of the electronic structures of cluster compounds clearly limits our intent to tether the principles of reactivity and bonding. The highest success is expected to occur for dinuclear compounds, but to fall off rapidly with increasing nuclearity.

2. FORMATION OF METAL–METAL BONDS

2.1. From Mononuclear Compounds by Coupling Reactions

2.1.1. Involving Metal Centered Radicals

A large number of ligand substitution reactions of dinuclear metal carbonyl compounds have been shown to proceed via initial homolytic dissociation of the metal–metal bond. These are discussed in detail in Section 3.1.1. The radical mononuclear fragments are known to recombine. However, the number of synthetically useful or well documented reactions that involve the thermally, photolytically or chemically induced generation of metal centered radicals by homolysis of M–X bonds followed by coupling to generate M–M bonds, as shown in Equation 1, is very small indeed.

$$L_nM-X \rightarrow L_nM^\bullet + X^\bullet$$

(1)

$$2L_nM^\bullet \rightarrow L_{2n}M_2$$
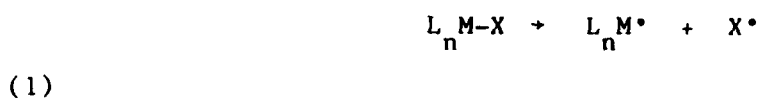
The reason for this appears to be that the coupling of two mononuclear fragments can, in most cases, occur by other more favorable pathways. Thus, although the preparation of $Cp_2W_2(CO)_6$ by thermolysis of $CpW(CO)_3CH_2Ph$ (40) may involve initial generation of $CpW(CO)_3$ and $PhCH_2^\bullet$ followed by dimerization, a reductive-coupling mechanism is more likely since $PhCH_2CH_2Ph$, not toluene, is formed. This ambiguity is discussed in more detail in Section 2.1.3.

By far, the most numerous reactions leading to coupling of neutral mononuclear compounds involve an initial dissociation or migration of a ligand as seen in the following sections, 2.1.2 and 2.1.3.

2.1.2. Involving Initial Ligand Dissociation Reactions

The most common example involves the loss of CO from a metal carbonyl complex. This may be achieved by thermolysis, photolysis or may be chemically induced by addition of a reagent such as Me_3NO. In the absence of coordinating ligands, the unsaturated metal species produced, normally having a 16 valence shell of electrons, can react to form metal-metal bonds. This is illustrated by the well known reactions 2 and 3 (41).

(2)
$$2Fe(CO)_5 \xrightarrow[\text{or } h\nu]{\Delta} Fe_2(CO)_9 + CO$$

(3)
$$3Ru(CO)_5 \xrightarrow{50\,^\circ C} Ru_3(CO)_{12} + 3CO$$
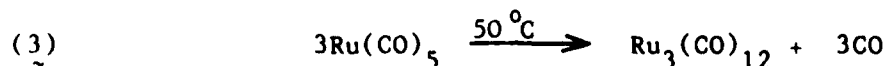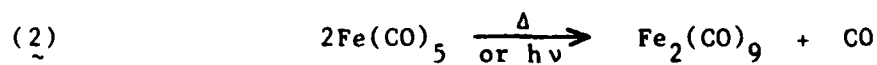
However, the generation of a highly unsaturated metal center does not always lead to metal-metal bond formation, as is seen in the photolysis of the group 6 transition metal carbonyls $M(CO)_6$ (M = Cr, Mo, W). Even in hydrocarbon solvents, solvento species of formula $M(CO)_5-(S)$ are formed (42), and generation of dinuclear compounds $M_2(CO)_{10}$ (M=M) is not observed.

Other examples of the formation of M-M bonds, which proceed by an initial CO dissociation, are seen in reactions 4 and 5 (43).

$$(4) \qquad 2CpV(CO)_4 \xrightarrow{h\nu} Cp_2V_2(CO)_5 + 3CO$$

$$(5) \qquad 2Fe(CO)_3(\eta^4-C_4H_4) \xrightarrow{h\nu} (\eta^4-C_4H_4)_2Fe_2(CO)_3 \ (M\equiv M) + 3CO$$
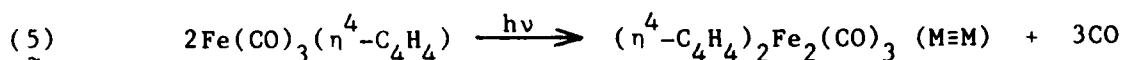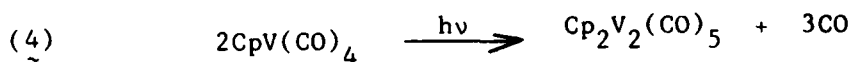
Aside from CO loss, a number of other ligands are known to dissociate to generate unsaturated metal species, which then react to form M-M bonds. For example, PPh_3 is lost by thermolysis of $Pt(PPh_3)_3$ and ethylene is lost from $Pt(PPh_3)_2(C_2H_4)$ to yield dinuclear and trinuclear products, I and II, which were shown by X-ray studies to contain Pt-Pt bonds (44).
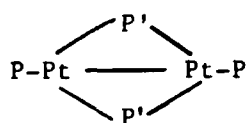
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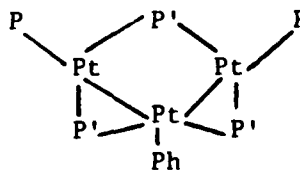
II

where P = PPh_3 and P' = PPh_2

2.1.3. Involving Elimination Reactions: Reductive Coupling

In certain circumstances, reductive coupling, also called reductive elimination and defined by the generalized equation 6, can be an unfavora-

ble process. This appears to be the case when an unstable, highly energetic metal fragment would be formed. Intermolecular reductive-coupling can then provide a more favorable pathway, since concommitant formation of a M-M bond can lead to a stable dinuclear product in $\underset{\sim}{7}$.

$$(6) \qquad L_nM\diagdown_R^X \quad \rightarrow \quad L_nM \quad + \quad R\text{-}X$$

$$(\underset{\sim}{7}) \qquad L_nM\text{-}R \quad + \quad X\text{-}ML_n \quad \rightarrow \quad M_2L_{2n} \quad + \quad R\text{-}X$$

Mechanistically, one of the best studied systems is the thermal decomposition of tertiaryphosphine gold(I) alkyl compounds, $(R'_3P)AuR$. When $MeAuPPh_3$ is heated at $100^{\circ}C$ in decalin, a first order generation of ethane is observed and the sequence shown in $\underset{\sim}{8}$ has been proposed (45). A gold mirror is deposited due to the instability of $[Au_2L]$.

$$MeAuL \quad \rightarrow \quad MeAu \quad + \quad L$$
$$(\underset{\sim}{8})$$
$$MeAu \quad + \quad MeAuL \quad \rightarrow \quad EtH \quad + \quad [Au_2L]$$
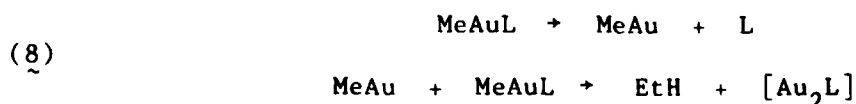
The lack of production of methane, even in the presence of H-donor solvents, rules out homolysis of the Au-Me bond. The formation of ethane is inhibited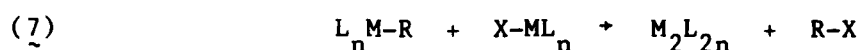 by added phosphine, which clearly supports the view that initial phosphine ligand dissociation is required to generate an unsaturated metal center. This has been shown to be important in all reductive coupling reactions and normally results in first order kinetics.

The reductive-coupling mechanism has been used to explain the observation that the decomposition of transition metal monoalkyl compounds containing β-hydrogen atoms can lead to a mixture of alkane and alkene. For example, decomposition of the n-octyl iridium complex $Ir(n\text{-}octyl)(CO)(PPh_3)_2$, generates both 1-octene and octane, though the Ir-Ir dimer or cluster complex was not identified (46).

The reductive-coupling reaction involving a metal-hydride and a metal-alkyl complex has been used to generate heterodinuclear compounds, e.g. as in reaction $\underset{\sim}{9}$ (47).

(9) $HMn(CO)_5 + MeAuPPh_3 \rightarrow (CO)_5MnAuPPh_3 + CH_4$

The work of Norton et al. (48) has clearly shown that cis-$Os(CO)_4$-(R)(H) compounds undergo intermolecular reductive coupling, despite the fact that R-H coupling is normally much more facile than either R-R or H-H coupling from mononuclear complexes. Presumably, the $Os(CO)_4$ fragment that would be generated by an intramolecular elimination of R-H is too unstable (too highly energetic) and thus, the much more circuitous bimolecular reaction pathway shown in $\underset{\sim\sim}{10}$ occurs. Once again, the rate determining step is generation of an unsaturated 16 valence shell electron species, which in this case, involves alkyl migration to give an acyl intermediate.

$$Os(CO)_4(H)(Me) \rightarrow Os(CO)_3H(C(O)CH_3)$$

($\underset{\sim\sim}{10}$)

$$Os(CO)_3H(C(O)CH_3) + Os(CO)_4(H)(CH_3) \rightarrow Os_2(CO)_8(H)(CH_3) + CH_4$$
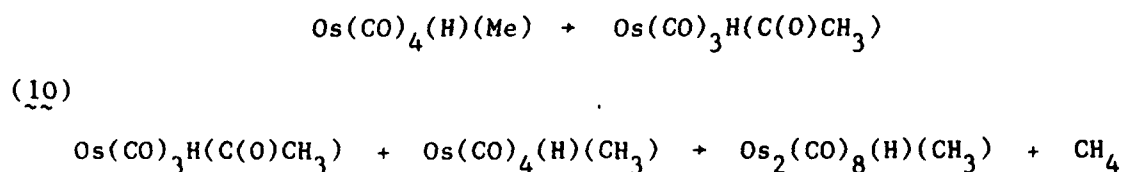
In the decomposition of cis $H_2Os(CO)_4$, initial loss of CO takes place to generate a vacant coordination site whereby a bimetallic pathway becomes possible: equation $\underset{\sim\sim}{11}$.

$$H_2Os(CO)_4 \rightarrow H_2Os(CO)_3 + CO$$

($\underset{\sim\sim}{11}$) $H_2Os(CO)_3 + H_2Os(CO)_4 \rightarrow "H_2Os_2(CO)_7" + H_2$

$$H_2Os_2(CO)_7 + CO \rightarrow H_2Os_2(CO)_8$$
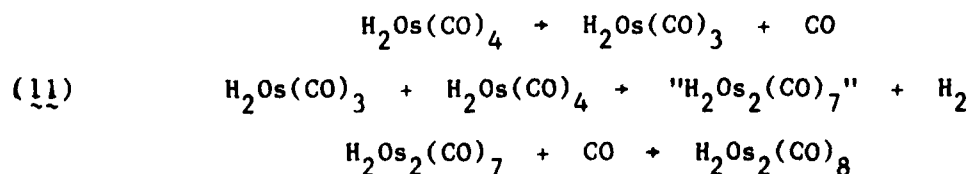
Rather interestingly, the ability of transition metal ions to catalyze the dimerization of methyl radicals was proposed to occur by initial formation of monomethyl complexes, followed by reductive coupling, equation 12, over two decades ago (49).

$$CH_3 + M \rightarrow CH_3-M$$

(12)

$$2CH_3-M \rightarrow CH_3CH_3 + 2M$$
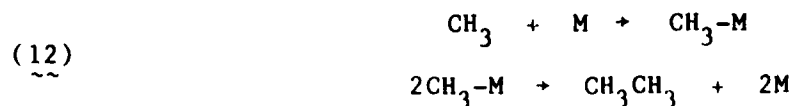
The mechanism of formation of the dinuclear homoleptic carbonyls of cobalt, manganese and rhenium from their respective mononuclear hydrides is uncertain. The reverse reaction, hydrogenation of the dinuclear carbonyls, has been much studied and two different pathways have been proposed. See equations 13 and 14.

$$M_2(CO)_{2x} \underset{}{\overset{h\nu}{\rightleftarrows}} 2M(CO)_x$$

$$M(CO)_x \rightleftarrows M(CO)_{x-1} + CO$$

(13)

$$M(CO)_{x-1} + H_2 \rightarrow H_2M(CO)_{x-1}$$

$$M(CO)_x + H_2M(CO)_{x-1} \rightarrow HM(CO)_x + HM(CO)_{x-1}$$

$$HM(CO)_{x-1} + CO \rightarrow HM(CO)_x$$
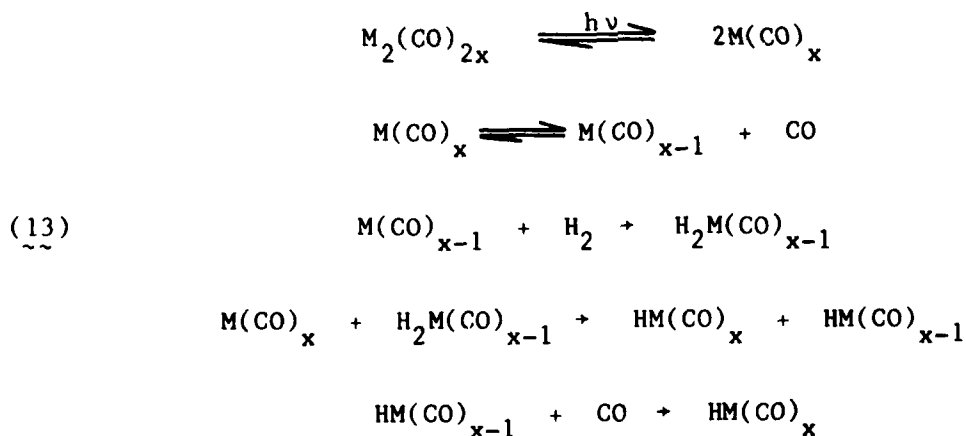
In the reaction sequence shown in 13, an initial reversible M-M bond homolytic cleavage is followed by a loss of a carbonyl ligand to generate a reactive 15 valence shell electron species which picks up hydrogen. It appears that this sequence occurs for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (50).

$$M_2(CO)_{2x} \xrightarrow{\ h\nu\ } M_2(CO)_{2x-1} + CO$$

$$M_2(CO)_{2x-1} + H_2 \rightarrow H_2M_2(CO)_{2x-1}$$

(14)

$$H_2M_2(CO)_{2x-1} \rightarrow HM(CO)_x + HM(CO)_{x-1}$$

$$HM(CO)_{x-1} + CO \rightarrow HM(CO)_x$$
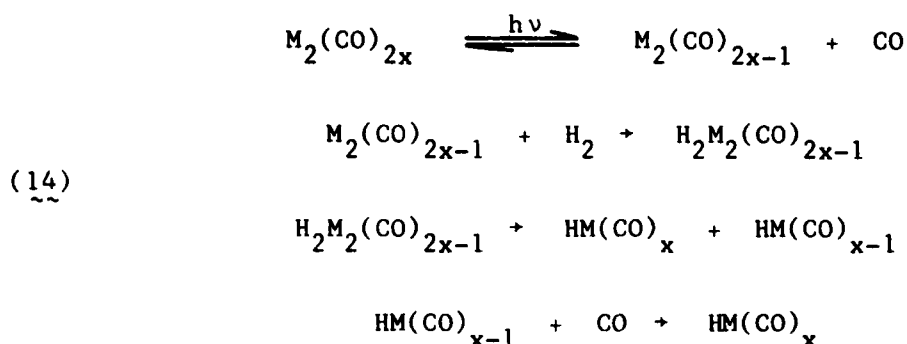
The sequence described in 14 may well occur for hydrogenation of $Co_2(CO)_8$ (51). A reverse of the third step would be reductive-coupling and it has been suggested (52) that this type of step occurs in the $Co_2(CO)_8$ catalyzed hydroformylation of olefins. See reaction 15.

(15) $$HCo(CO)_4 + RC(O)Co(CO)_3 \rightarrow Co_2(CO)_7 + RCHO$$
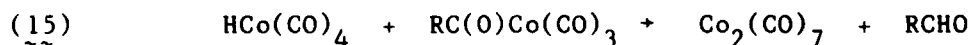
2.2. By Bimolecular Displacement Reactions

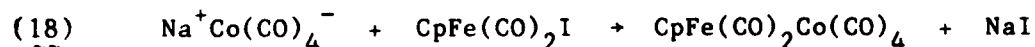This method (53,54) offers great potential for the systematic synthesis of dinuclear and higher nuclearity carbonyl compounds. A typical reaction between a carbonylate anion and metal carbonyl halide is seen in equation 16. This method is also one of the cleanest for the preparation of heterodinuclear metal-metal bonds, as is seen by the reactions 17 and 18.

(16) $$Na^+Mn(CO)_5^- + BrMn(CO)_5 \rightarrow Mn_2(CO)_{10} + NaBr$$

(17) $$Na^+Mn(CO)_5^- + BrRe(CO)_5 \rightarrow (CO)_5MnRe(CO)_5 + NaBr$$

(18) $$Na^+Co(CO)_4^- + CpFe(CO)_2I \rightarrow CpFe(CO)_2Co(CO)_4 + NaI$$
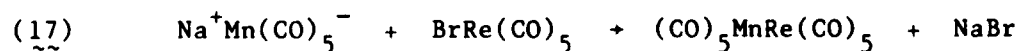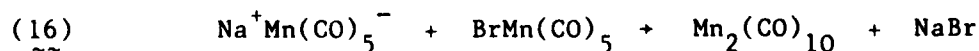
Geoffroy and coworkers (55,56) have shown that mononuclear carbonylate anions will react with polynuclear carbonyl compounds with the expulsion

of CO. Subsequent protonation has led to the synthesis of a range of hydrido carbonyl mixed metal cluster compounds, some of which are outlined by equations 19, 20 and 21.

(19) $\quad Ru_3(CO)_{12} + Fe(CO)_4^{2-} \xrightarrow{\Delta} \xrightarrow{H^+} H_2FeRu_3(CO)_{13}$

(20) $\quad Ru_2Os(CO)_{12} + Fe(CO)_4^{2-} \xrightarrow{\Delta} \xrightarrow{H^+} H_2FeRu_2Os(CO)_{13}$

(21) $\quad RuOs_2(CO)_{12} + Fe(CO)_4^{2-} \xrightarrow{\Delta} \xrightarrow{H^+} H_2FeRuOs_2(CO)_{13}$
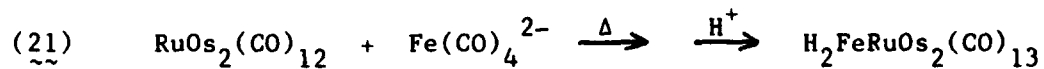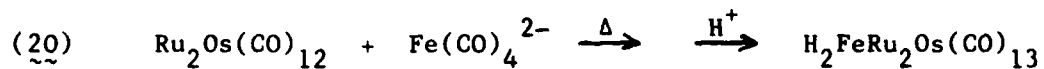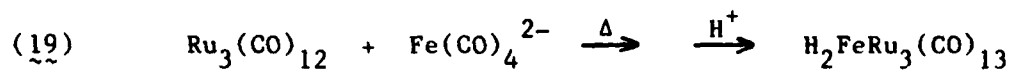
The full potential of these types of displacement reactions remains to be established, but appears very promising in its general applicability.

2.3. By Addition of a Metal Complex or Fragment Across an M-X Multiple Bond

This synthetic approach has been most elaborately demonstrated by Stone and coworkers at Bristol. They reasoned that C=M and C≡M bonds should react with low valent or coordinatively unsaturated metal complexes as do C=C and C≡C linkages. The generalized reactions that might be anticipated are 22 for additions to metal carbenes and 23 for additions to carbynes.

(22)

$$M=C\diagdown \quad + \quad M' \quad \rightarrow \quad M\text{------}M'$$

(23)

$$M\equiv C- \quad + \quad M' \quad \rightarrow \quad M\text{------}M' \quad \text{or} \quad M\text{------}M'$$
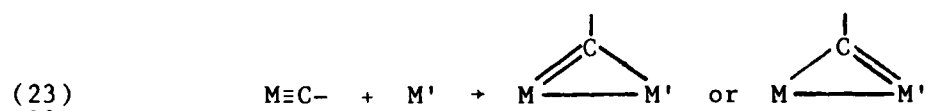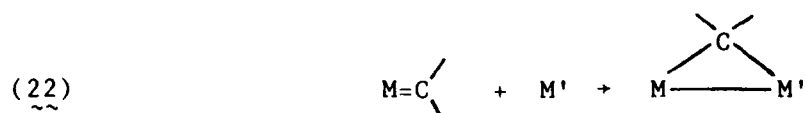
These reactions have led to an enormous group of new dinuclear bridged carbene or carbyne compounds, which are illustrated by (III) through (XIV) (R = p-tolyl), and having all been reported within the last year or so (57,58,59,60), they surely must represent the "tip of the iceberg" with regard to what can be achieved by this synthetic strategy.

The bridging alkylidyne ligand in the compounds formed by reaction 23 can be used to prepare triangulo-metal complexes with capping μ_3-CR ligands as is schematically shown in 24.

(24)

$$M\text{------}M' \quad + \quad M'' \quad \rightarrow \quad M\text{------}M'$$
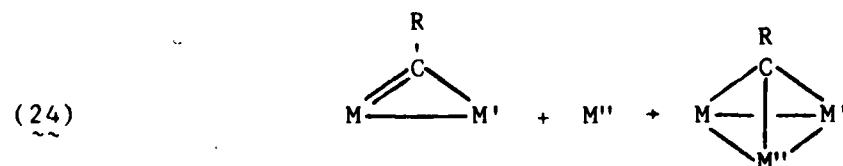
The compounds (XV) and (XVI) have been prepared in this manner and structurally characterized (61).

$$\underset{(OC)_5W}{\overset{Ph\diagdown C \diagup OMe}{\diagup\diagdown}}\underset{Pt(PMe_3)_2}{}$$

(III)

$$\underset{(OC)_5Mo}{\overset{Ph\diagdown C \diagup OMe}{\diagup\diagdown}}\underset{Pt(PMe_2Ph)_2}{}$$

(IV)

$$(OC)_5Cr \underset{}{\overset{O\diagdown C}{\diagup\diagdown}} Pt(PMe_2Ph)_2$$

(V)

$$\underset{(OC)_5W}{\overset{Ph\diagdown C \diagup Ph}{\diagup\diagdown}}\underset{Pt(PMe_3)_2}{}$$

(VI)

$$\underset{(\eta-C_5H_5)(OC)_2Mn}{\overset{Ph\diagdown C \diagup OMe}{\diagup\diagdown}}\underset{Ni(PMe_3)_2}{}$$

(VII)

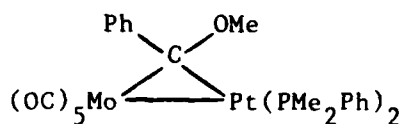$$\underset{(\eta-C_5H_5)(OC)_2Mn}{\overset{Ph\diagdown C \diagup OMe}{\diagup\diagdown}}\underset{Pd(PMe_3)_2}{}$$

(VIII)

$$\underset{(\eta-C_5H_5)(OC)_2Re}{\overset{MeO\diagdown C \diagup R}{\diagup\diagdown}}\underset{Pt(PMe_3)_2}{}$$

(IX)

$$\underset{(OC)_4(Br)W}{\overset{R\diagdown C}{\diagdown\diagup}}\underset{Pt(PMe_3)_2}{}$$

(X)

$$(\eta-C_5H_4Me)(OC)_2Mn \underset{}{\overset{R\diagdown C}{\diagdown\diagup}} W(CO)_2(\eta-C_5H_5)$$

(XI)

$$(\eta-C_6Me_6)(OC)Cr \underset{\underset{O}{C}}{\overset{R\diagdown C}{\diagup\diagdown}} W(CO)_2(\eta-C_5H_5)$$

(XII)

$(\eta-C_9H_7)(OC)Rh \underset{}{\overset{R}{C}} W(CO)_2(\eta-C_5H_5)$

(XIII)

$(\eta-C_5H_5)Co \underset{C}{\overset{R}{C}} W(CO)_2(\eta-C_5H_5)$

(XIV)

$(\eta-C_5H_5)(OC)_2W \underset{Fe}{\overset{R}{C}} Rh(\eta-C_9H_7)$

(XV)

$(\eta-C_5H_5)(OC)_2W \underset{Fe}{\overset{R}{C}} Pt(CO)(PEt_3)$

(XVI)

(XVII) (M = Ni)
(XVIII) (M = Pt)

$(\eta-C_5H_5)(OC)_2W \underset{Co}{\overset{R}{C}} Co(CO)_3$

(CO)$_3$

(XIX)

$(\eta-C_5H_5)(OC)_2W \underset{Rh}{\overset{R}{C}} Rh(\eta-C_5Me_5)$

$(\eta-C_5Me_5)$
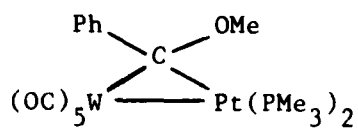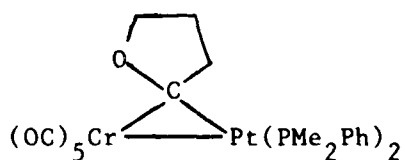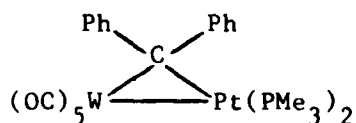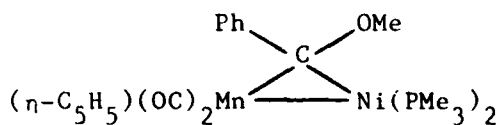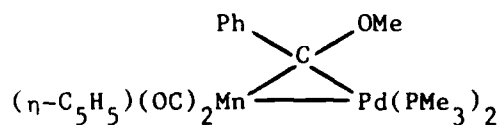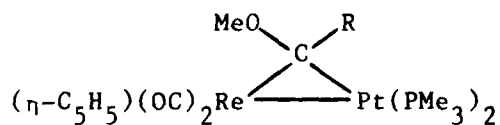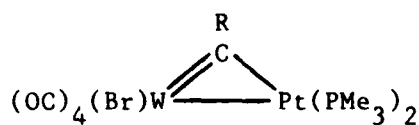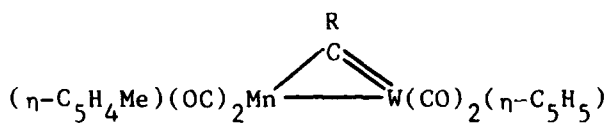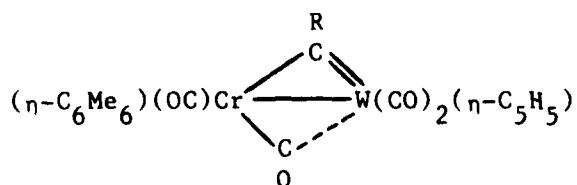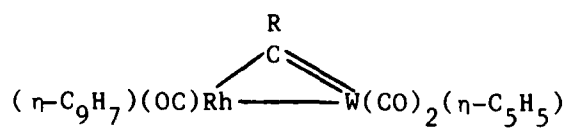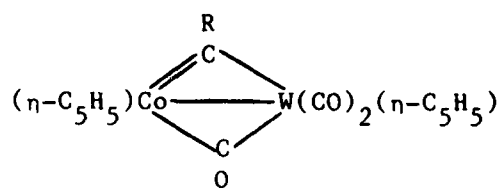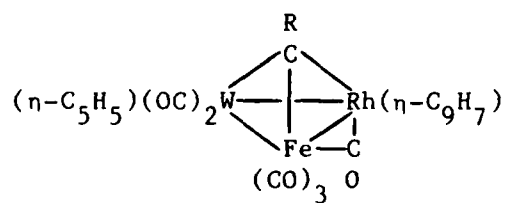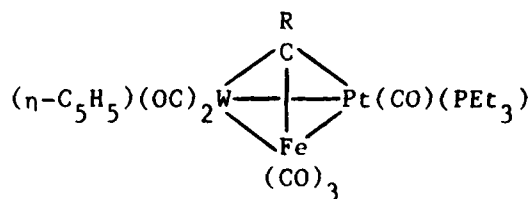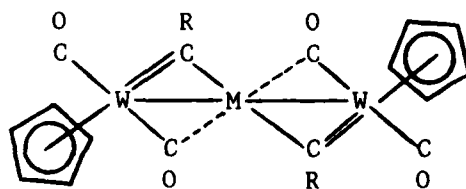
(XX)

The reaction between p-tolyl-C≡W(CO)$_2$Cp and Ni(COD)$_2$ and Pt(C$_2$H$_4$)$_3$ afforded (XVII) and (XVIII), respectively.

Recognizing that the W(CO)$_2$Cp fragment is isolobal with RC≡ (62), Stone and coworkers were prompted to react Co$_2$(CO)$_8$ and Rh$_2$(μ-CO)$_2$(C$_5$-Me$_5$)$_2$ with the alkylidene compound p-tolyl-C≡W(CO)$_2$Cp. They obtained the alkylidine capped triangulo compounds (XIX) and (XX), which are analogous to alkyne adducts of these dimetal centers (61).

These and other reactions of the Stone group have been reviewed (63).

Although all of the aforementioned examples involve organometallic systems, it is not unreasonable to suppose the principles could readily be extended to more conventional coordination compounds. Indeed the reactions between MoO(OR)$_4$ and Mo$_2$(OR)$_6$ (M≡M) compounds give (64) Mo$_3$-(μ$_3$-O)(OR)$_{10}$ compounds, which are triangulo compounds of the type noted in Table 1.2.

2.4. By Reduction of Mononuclear Metal Halides

For transition metals with odd numbers of valence electrons, the attainment of an electron precise structure requires the presence of M-M bonds in neutral, homoleptic binary carbonyl compounds. Hence the preparation of carbonyl compounds by reduction of metal halides provides a common route to dinuclear or polynuclear metal-metal bonded compounds. The reducing agent may be CO, Na, the metal itself or some other electropositive metal, or even the solvent. This simple route to metal-metal bonded carbonyls is particularly effective for the cobalt triad (65,66,67) as is seen in reactions 25, 26, 27 and 28.

$$(25) \qquad 2CoI_2 \; + \; 8CO \; + \; 4Cu \; \rightarrow \; Co_2(CO)_8 \; + \; 4CuI$$

$$(26) \qquad RhCl_3 3H_2O \; \xrightarrow[\text{MeOH, }60^\circ C]{\text{CO, 50 Atmos}} \; Rh_6(CO)_{16}$$

$$(27) \qquad IrCl_3 3H_2O \; \xrightarrow[\text{MeOH, }60^\circ C]{\text{CO, 50 Atmos}} \; Ir_4(CO)_{12}$$

$$(28) \qquad [Rh(CO)_2Cl]_2 \; \xrightarrow[\text{NaHCO}_3]{\text{CO}} \; Rh_4(CO)_{12}$$
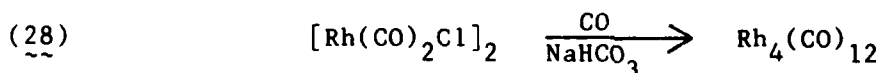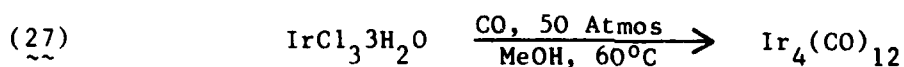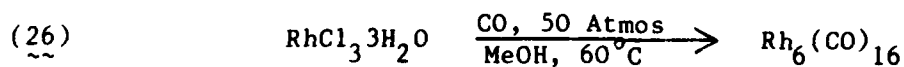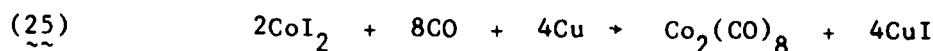
One of the largest classes of polynuclear cluster carbonyls are formed by the reduction of the hexachloroplatinate anion, $PtCl_6^{2-}$, with CO in the presence of base according to the generalized equation 29.

$$(29) \qquad 3n[PtCl_6^{2-}] \; + \; (12n+1)CO \; + \; (12n+2)OH^- \; \rightarrow$$
$$[Pt_3(CO)_6]_n^{2-} \; + \; 18nCl^- \; + \; (6n-1)CO_2 \; + \; (6n+1)H_2O$$
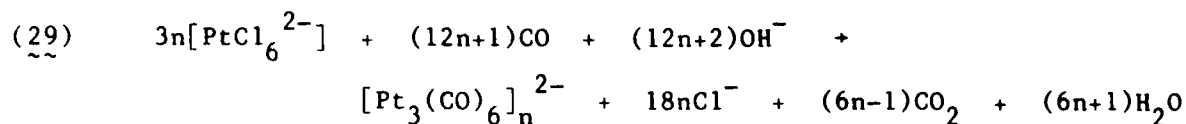
The value of n may be controlled by varying the amount of base, and values from n = 2 to n = 12 have been identified (68).

For early transition metals, partial reduction of penta- or hexa-halides (group 5 and 6 elements) can lead to lower valent compounds containing metal-metal bonds. These may be cluster compounds with delocalized M-M bonds or dinuclear compounds with multiple bonds.

For example, reduction of WCl_6 can lead to polymeric WCl_4. Further reduction by Na/Hg in THF leads first to $W_2Cl_6(THF)_4$ and then to W_2Cl_4-$(THF)_4$. This has recently proved a good method of entry into the chemistry of W-W quadruple bonds (69,70).

In a similar manner, reduction of $TaCl_5$ using Na/Hg (2 equiv) in the presence of tetrahydrothiophene, THT, gives a d^2-d^2 dimer of tantalum-(III), $Ta_2Cl_6(THT)_3$, which has a face shared bioctahedral geometry, with two chloro groups and one sulfur atom of the THT ligand forming the

bridge (71). Recently Sattleberger and Wilson have shown that reduction of $TaCl_5$ by Na/Hg (2 equiv) in the presence of added PMe_3 yields a tantalum d^2-d^2 dimer $Ta_2Cl_6(PMe_3)_4$ (72).

In the absence of coordinating ligands, polynuclear cluster halides can be formed, e.g. $[M_6Cl_8]Cl_4$ where M = Mo and W and $[M_6Cl_{12}]Cl_2$ where M = Nb and Ta (73).

Addition of coordinating ligands to polymeric halides can sometimes lead to the formation of discrete molecules containing M–M multiple bonds, e.g. β–$MoCl_2$ and pyridine react to give $Mo_2Cl_4(py)_4$ (M$\equiv$M) (74).

2.5. By Metathetic Reactions Involving Polymeric Transition Metal Halides

Metathetic reactions involving organolithium reagents and polymeric halides of molybdenum and tungsten often proceed to yield discrete metal–metal bonded dimers as is shown in reactions 30 and 31 (75,76)

(30) $\qquad [MoCl_3]_x + 3xLiNMe_2 \rightarrow Mo_2(NMe_3)_6 + LiCl$

(31) $\qquad [WCl_4]_x + 4xLiNMe_2 \rightarrow W_2(NMe_2)_6 + W(NMe_2)_6 + LiCl$
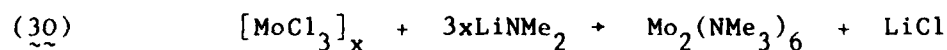
These types of reactions may lead to a variety of products, particularly when the organic group can itself react to generate new ligands. For example, the reaction between $MoCl_5$ and $LiCH_2SiMe_3$ (5 equiv) yields a mixture of $Mo_2(CH_2SiMe_3)_6$ (M$\equiv$M), $(MeSiCH_2)_3Mo=CHSiMe_3$ and $(Me_3SiCH_2)_3$–M$\equiv$CSiMe_3$ (77). The formation of alkylidene and alkylidyne ligands may arise from α–hydrogen abstraction reactions (78), though the detailed nature of the metathetic reactions is unknown.

It had been suggested (79) that the dinuclear compounds might arise from the coupling of two reactive mononuclear species, equation 32, where

M = Mo or W and L = NMe$_2$ or CH$_2$SiMe$_3$. However, on the basis of a number

of cross-over experiments, such a coupling scheme has been discounted

(80). It seems that the dinuclear M-M multiple bonded compounds arise

from substitution reactions at cluster metal halide species which finally

yield expulsion of dinuclear fragments.

(32) $$2ML_3 \rightarrow L_3M\,ML_3$$

2.6. By Oligomerization of Compounds with M-M Bonds

Currently it is not known what factors influence the preference for

multiple bonding (M-M) versus delocalized cluster bonding. Two factors

which are clearly important are steric factors and ligand lability.

McCarley et al. (81) showed that it was possible to couple Mo-Mo

quadruple bonds to form a rectangular Mo$_4$ cluster by an elimination of

four labile ligands (MeOH) as is shown in reaction 33. The Mo-to-Mo

distances in the Mo$_4$ cluster are 2.211(3) and 2.901(2) Å, which may be

reasonably taken to represent Mo-to-Mo triple and single bonds, respec-

tively.

(33)
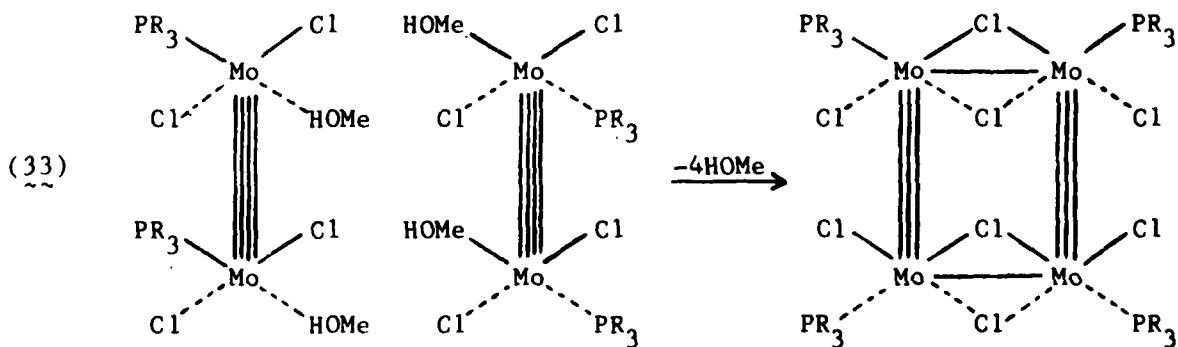
Replacement of two OBu^t ligands in Mo$_2$(OBu^t)$_6$ (M≡M) by two fluoride

ligands leads to dimerization to give a tetranuclear compound Mo$_4$F$_4$-

$(OBu^t)_8$ (82). However in this case, the Mo_4 unit is a bisphenoid having two short Mo–Mo distances (2.26 Å) and four long distances (3.75 Å (averaged)) corresponding to Mo–Mo triple bond and non-bonding distances, respectively. The dimerization occurs without influencing the ground state properties of the Mo–Mo triple bond and the reaction may be understood in terms of the effect of replacing $Bu^t O$ ligands by the smaller and more electronegative fluoride ligands which promotes a Lewis base association reaction. That this should occur by fluoride bridge formation, rather than alkoxide bridge formation is perhaps unexpected. See Figure 2.1.

The influence of steric factors is also seen in the coordination chemistry of molybdenum annd tungsten alkoxides. Bulky ligands, e.g. $Bu^t O$ and $Pr^i O$, favor dinuclear compounds, $M_2(OR)_6$ (83,84) or $Mo_2(OPr^i)_8$ (85), while less bulky ligands favor oligomers $[M(OR)_3]_n$ and $[M(OR)_4]_n$. The structure of $W_4(OEt)_{16}$ has recently been determined (39) and is shown in Figure 2.2. The centrosymmetric molecule contains a planar M_4 unit with three unique M–M bonding distances which are 2.645(2), 2.763(2) and 2.936(2) Å. Clearly, the eight electrons contributed by the four tungsten-(IV) ions are involved in cluster bonding. In view of the structure of $Mo_2(OPr^i)_8$ (M≡M), the W_4 unit in $W_4(OEt)_{16}$ may be viewed, albeit rather fancifully, as two M–M double bonds coupled through the agency of alkoxy bridges in the manner shown in equation 34.

(34)   M=M + M=M →
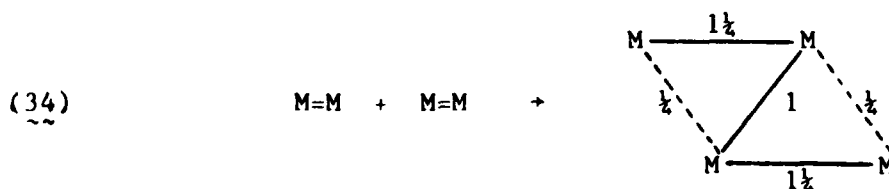
Figure 2.1. An ORTEP view of the central $Mo_4(\mu-F)_4(OC)_8$ skeleton of the $Mo_4F_4(OBu^t)_8$ molecule.

Figure 2.2. An ORTEP view of the centrosymmetric $W_4(OEt)_{16}$ molecule.

Labels visible in the figure: O(2I)', O(6)', O(8)', O(24)', O(I2)', O(I5), W(2)', O(3)', C(II), C(I0), O(9), O(I5), C(I6), C(I7), O(9)', O(3), W(I), O(I2), O(4), C(5), O(6), C(I3), C(I4), C(25), O(24), W(2), C(7), C(8), C(26), C(I9), O(I8), O(2I), C(22), C(20), C(23)
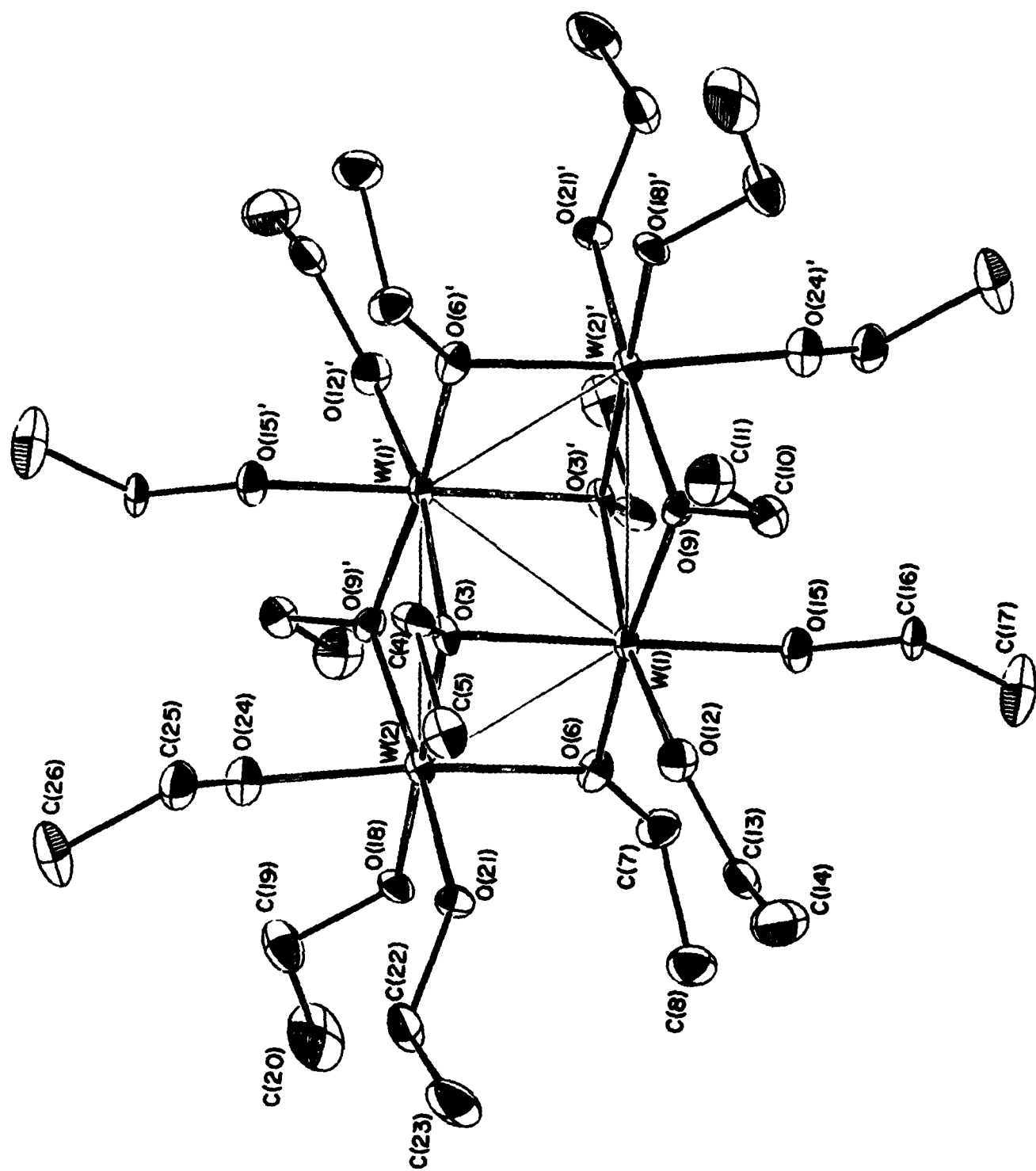
The work of Lewis *et al*. (86) has shown that thermolysis of Os_3-$(CO)_{12}$ can generate a number of higher nuclearity clusters, equation 35, and related thermolysis reactions are well known for other polynuclear carbonyls (4). The initial step in these reactions probably involves loss of CO, but a large number of other processes are probably taking place, including M-M homolysis.

(35) $\quad Os_3(CO)_{12} \xrightarrow[\text{12h}]{195^\circ - 200^\circ C}$

$\qquad Os_4(CO)_{13} + Os_5(CO)_{16} + Os_7(CO)_{21} + Os_8(CO)_{23} + Os_8(CO)_{21}C$
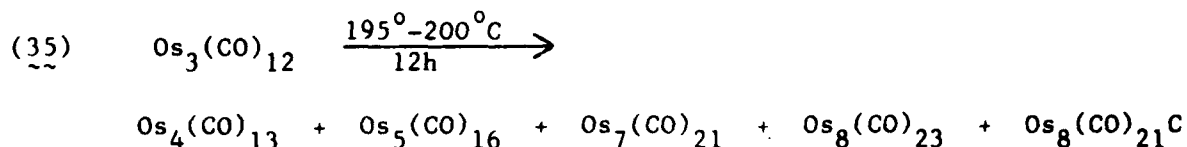
The thermolysis of a mixture of metal carbonyls can lead to mixed metal clusters (87) as shown in reaction 36, but the mechanism is unknown and this type of synthesis does not generally allow the prediction of products.

(36) $\qquad Fe_2(CO)_9 + CpCo(CO)_2 \rightarrow Fe_2CoCp(CO)_9$

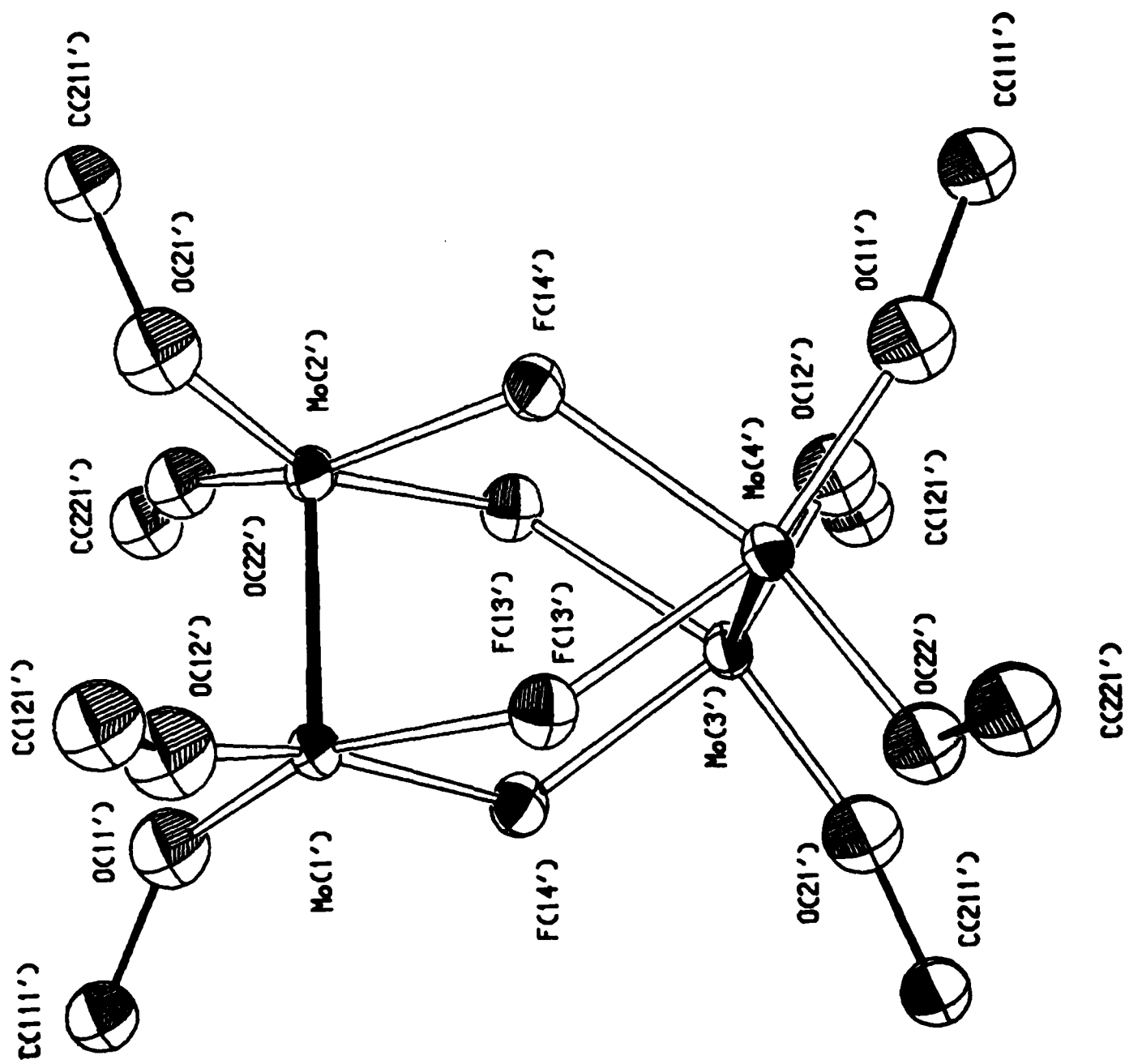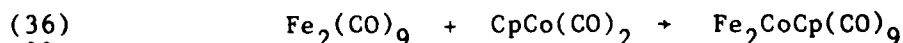An intriguing conversion of a dinuclear compound, $Re_2(OAc)_4X_2$ to a trinuclear compound, Re_3X_9, by the addition of HX to the former, where X = Cl, Br (74) and I (88), has been reported by Walton and coworkers. The reorganization of metal-metal bonds is most remarkable, 37, though the pathway is not known.

(37) $\qquad 3Re\equiv Re \rightarrow 2$

2.7. By Addition of Low Valent Metal Compounds Across Metal-Metal Multiple Bonds

The processes represented by 38 and 39 provide two possibilities

for the introduction of an unsaturated metal fragment M' to a dinuclear or trinuclear center.

(38) $\quad\quad\quad\quad\quad$ M=M + M' →

(39)
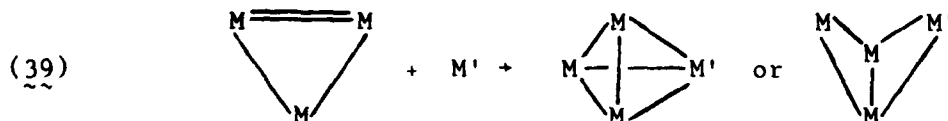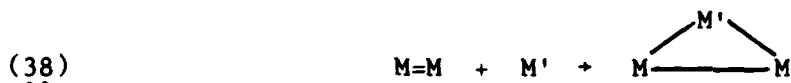
Stone and coworkers have demonstrated that this is indeed a viable systematic route to new cluster compounds as is seen in the following (89,90).

The compound $(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu_2\text{-}CO)_2$, which contains a metal-to-metal double bond (91) reacts with nickel and platinum bis-1,5-cycloocta-diene compounds to give triangulo $[Rh_2M]$ compounds according to equation 40 (M = Ni or Pt).

(40) $\quad (\eta^5\text{-}C_5Me_5)_2Rh_2(\mu_2\text{-}CO)_2 + M(COD)_2 \rightarrow (\eta^5\text{-}C_5Me_5)_2Rh_2M(\mu\text{-}CO)_3(COD)$
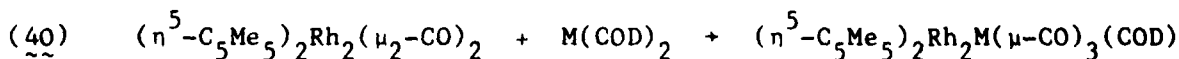
By the addition of either $Pt(C_2H_4)_2(PPh_3)$ or $Pt(C_2H_4)(PPh_3)_2$ to $(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu_2\text{-}CO)_2$, $(\eta^5\text{-}C_5Me_5)_2Rh_2Pt(\mu_3\text{-}CO)_2CO(PPh_3)$ was formed.

When $Re_2(\mu_2\text{-}H)_2(CO)_8$ (M=M) (92) was reacted with either $Pt(C_2H_4)_2$-$(PPh_3)_2$ or $Pt(C_2H_4)(PPh_3)_2$, the triangulo $[Re_2Pt]$ compound (XXI) was formed.

The compounds $Pt(C_2H_4)_2(PR_3)$, where $PR_3 = P(cyclo\text{-}C_6H_{11})_3$, PPh_3 or PBu^t_2Me, react with $Os_3(\mu_2\text{-}H)_2(CO)_{10}$ to yield "58-electron" clusters (XXII).
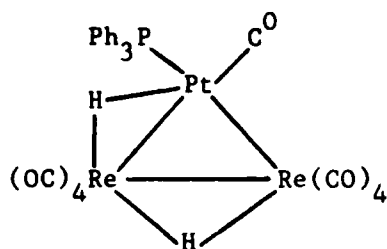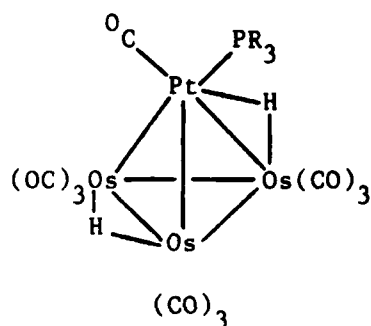
XXI   XXII

Similar types of additions to $Cp_2Mo_2(CO)_4$ ($M\equiv M$) (93) have been noted, but no products have yet been structurally characterized by X-ray studies (94).

2.8. Through the Use of Special Bridging Ligands

Bidentate ligands with small "bites" often prefer to bridge two metal atoms even in the absence of significant metal-metal bonding. This is well illustrated in the structures of copper(I) carboxylates (95). The relatively weak d^8-d^8 Rh(I)-Rh(I) bond (see Section 1.2.1 and Figure 1.1) can be "captured" through the agency of suitable bridging ligands which include diphosphinomethanes $R_2PCH_2PR_3$, diarsinomethanes $R_2AsCH_2AsR_2$ and $CN(CH_2)_3NC$ (21,96). Related Pt-Pt and Pd-Pd dimers have been prepared and collectively, the bonding in this group of compounds have been discussed by Hoffman and Hoffmann (97).

The use of specially tailored ligands for constructing binuclear complexes can be taken one step further by the use of heteroatom donors as is seen in the recent work of Balch (98). 2-Diphenylphosphinopyridine Ph_2Ppy has essentially all the P donor properties of triphenylphosphine

and readily forms square planar d^8 metal complexes such as <u>trans</u>-Rh(CO)Cl-$(Ph_2Ppy)_2$ and $PdCl_2(Ph_2Ppy)_2$. There is then the potential to capture a second metal, M', as shown in $\underset{\sim\sim}{41}$. The P-N donor ligand can switch to a head-to-tail configuration and this is seen in the conproportionation reaction $\underset{\sim\sim}{42}$. The Pd-Pd complex that is formed has the structure shown in XXIII.

(41)

$$Ph_2P \cdots (py) \qquad M \qquad + \ M' \ \to$$

(42) $Pd(Ph_2Ppy)_2Cl_2$ + $\tfrac{1}{2}Pd_2(dba)_3$ $\to$ $Pd_2(Ph_2Ppy)_2Cl_2$ + 3/2dba

where dba = dibenzylideneacetone)
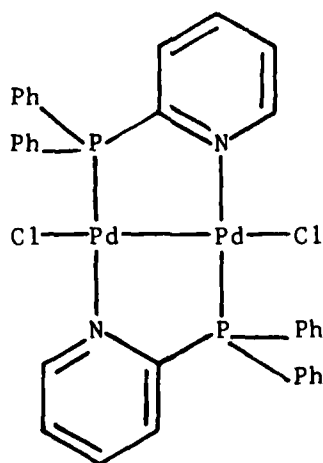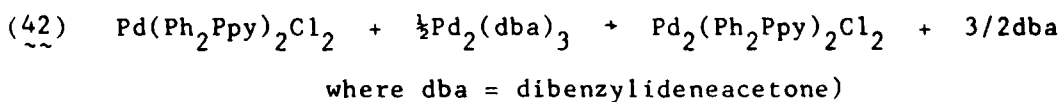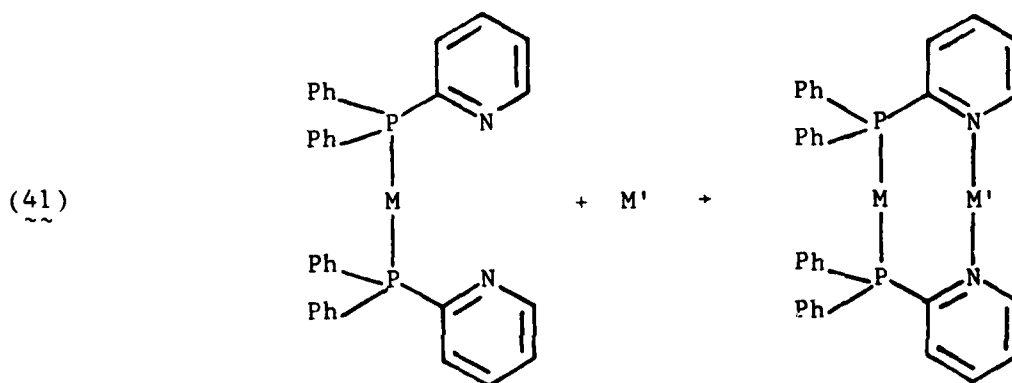
XXIII

The reaction between $Rh(CO)Cl(PPh_2py)_2$ with $(COD)PdCl_2$ yields $RhPd(Ph_2-Ppy)_2(CO)Cl_3$. The product has the rather surprising structure XXIV, which arises from oxidative addition of a Pd-Cl bond to the Rh center.
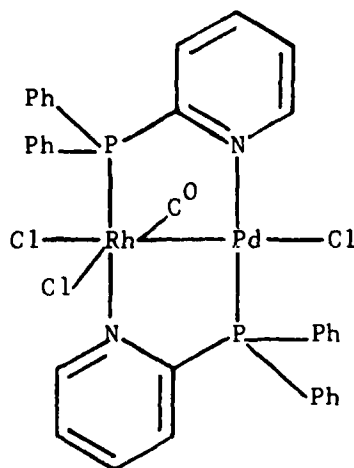
XXIV

From the reaction between $Ni(CO)_4$ and $CH(PPh_2)_3$ (tripod), a trinuclear product, $Ni_3(CO)_6$ (tripod) has been isolated (99). On the basis of spectroscopic data, the tripod ligand is believed to coordinate to each nickel atom as is shown in XXV.
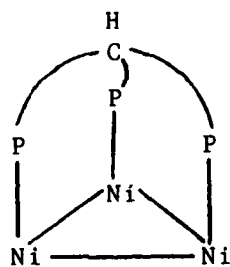
XXV

3. REACTIONS INVOLVING CHANGES IN METAL-METAL BOND ORDER

3.1. Cleavage of Metal-Metal Bonds

3.1.1. By Homolysis

A large number of dinuclear carbonyls and related organometallic compounds contain unbridged metal-metal single bonds. The thermal or photo induced population of the σ^* (antibonding) orbital by excitation of electrons from the σ (bonding) or other molecular orbitals would be expected to result in metal-metal bond cleavage. For these types of compounds, homolytic fission of the metal-metal bond is commonly observed and can provide the initial step for ligand substitution and other reactions.

A clear-cut example of a reversible homolysis of a metal-metal bond is seen in the chemistry of the d^7-d^7 dinuclear compound $Fe_2(\eta^3\text{-allyl})_2$-$(CO)_6$. At room temperature in hydrocarbon solvents, concentrations of the paramagnetic 17 electron monomer $Fe(\eta^3\text{-allyl})(CO)_3$ can be detected by e.s.r. spectroscopy (100). From variations of the concentration of monomer over the temperature range $+40^\circ$ to $-90^\circ C$, a value of ΔH = 13 Kcal mol^{-1} was calculated for the equilibrium, 43. This very low enthalpy value correlates well with the exceedingly long Fe-Fe bond length, 3.138(2) Å, found in the solid state (101).

(43) $\qquad Fe_2(\eta^3\text{-allyl})_2(CO)_6 \rightleftharpoons 2Fe(\eta^3\text{-allyl})(CO)_3$
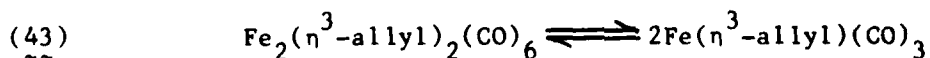
A room temperature, reversible homolysis of the Cr-Cr bond in $Cp_2Cr_2(CO)_6$ has also been proposed on the basis of nmr observations (102). Here too, in the solid state, an exceedingly long Cr-Cr bond distance, 3.281(1) Å, was found.

The related dinuclear compounds $Cp_2M_2(CO)_6$, where M = Mo and W, undergo thermal loss of CO with the formation of the M-M triply bonded compounds $Cp_2M_2(CO)_4$. By the thermolysis of a mixture of $Cp_2Mo_2(CO)_6$ and $Cp'_2Mo_2(CO)_6$, where $Cp' = MeC_5H_4$, Curtis and Klingler (94) have shown that initial homolysis of the Mo-Mo bond takes place to give the mononuclear fragments $CpMo(CO)_3$ and $Cp'Mo(CO)_3$ which lose CO and finally recombine to give triply bonded dimers. The resulting products are distributed statistically, equation 44.

(44) $Cp_2Mo_2(CO)_6 + Cp'_2Mo_2(CO)_6 \xrightarrow[-CO]{\Delta}$

$Cp_2Mo_2(CO)_4 + 2CpCp'Mo_2(CO)_4 + Cp'_2Mo_2(CO)_4$
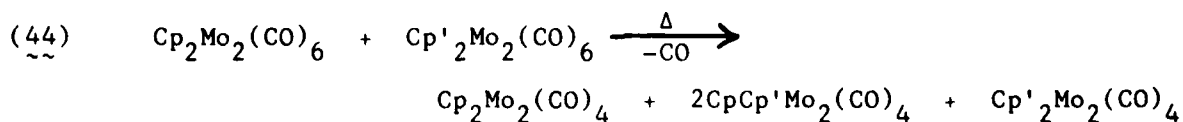
In separate experiments, it was shown that no scrambling of Cp/Cp' groups occurs once the triply bonded dimers are formed.

In the case of the d^7-d^7 dimers of manganese and rhenium, various reaction schemes have been proposed for substitution reactions based on kinetic observations. The substitution of PPh_3 by $P(OPh)_3$ has been extensively studied by Poe and coworkers (103,104,105) for the dinuclear compounds $M_2(CO)_8(PPh_3)_2$ (M = Mn and Re). These reactions have been proposed to proceed via an initial homolysis of the M-M bond, followed by substitution of the labile paramagnetic species formed as shown in the sequence 45.

$$Mn_2(CO)_8(PPh_3)_2 \rightleftharpoons 2Mn(CO)_4(PPh_3)$$

(45) $Mn(CO)_4(PPh_3) + P(OPh)_3 \rightarrow Mn(CO)_4(P(OPh)_3) + PPh_3$

$Mn(CO)_4(PPh_3) + Mn(CO)_4(P(OPh)_3) \rightarrow Mn_2(CO)_8(PPh_3)(P(OPh)_3)$
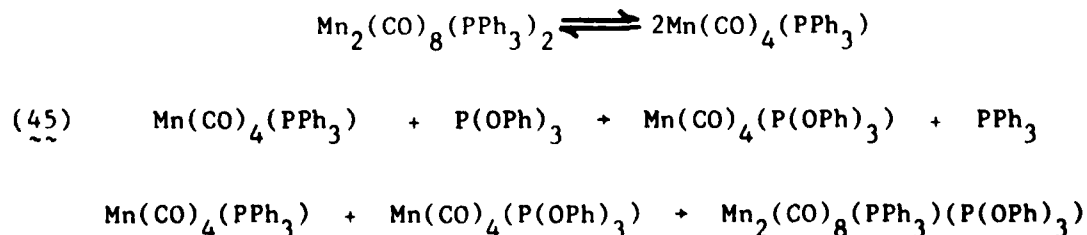
However, for the thermal reaction of $MnRe(CO)_{10}$ with PPh_3, PBu_3 and $P(OPh)_3$, the evidence supports a substitutional pathway proceeding via an initial loss of CO and not metal-metal bond fission. The key observation here is that no homodinuclear products are formed (106).

Brown and coworkers (107) have studied substitution reactions of $Co_2(CO)_8$ in great detail. With $AsPh_3$, $Co_2(CO)_7(AsPh_3)$ is initially formed, which reacts further to give $Co_2(CO)_6(AsPh_3)_2$. The rate of reaction is first order in $Co_2(CO)_8$, zeroeth order in $[AsPh_3]$, is suppressed by added [CO] and is not affected by molecular oxygen. A simple substitution pathway involving an initial loss of CO is clearly implicated, as shown in 46. The exchange reaction of $Co_2(CO)_8$ with *CO is believed to proceed in an analogous manner.

(46)
$$Co_2(CO)_8 \rightleftharpoons Co_2(CO)_7 + CO$$
$$Co_2(CO)_7 + L \rightarrow Co_2(CO)_7L$$
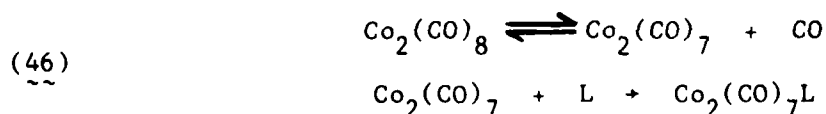
The reaction with PBu_3 is very fast by comparison and leads to ionic products $Co(CO)_3(PBu_3)_2^+Co(CO)_4^-$. The reaction with PPh_3 leads to analogous products, but the reaction is considerably slower and shows complex rate behavior as a function of temperature. The reaction is markedly inhibited by molecular oxygen and a radical chain process has been proposed, the key steps of which are shown in 47.

(47) (i) $$Co_2(CO)_8 + L \rightleftharpoons Co_2(CO)_8L$$

(ii) $$Co_2(CO)_8L \rightarrow Co(CO)_3L\cdot + Co(CO)_4\cdot + CO$$

(iii) $$Co(CO)_3L\cdot + Co_2(CO)_8 \rightarrow Co(CO)_3L^+ + Co_2(CO)_8^{\bar{\cdot}}$$

(iv) $$Co_2(CO)_8^{\overline{\cdot}} \rightarrow Co(CO)_4^{\cdot} + Co(CO)_4^{-}$$

(v) $$Co(CO)_3L^{+} + L \rightarrow Co(CO)_3L_2^{+}$$

(vi) $$Co(CO)_4^{\cdot} \rightleftharpoons Co(CO)_3 + CO$$

(vii) $$Co(CO)_3 + L \rightarrow Co(CO)_3L^{\cdot}$$

(viii) $$Co(CO)_4^{\cdot} + Co(CO)_3L^{\cdot} \rightarrow Co_2(CO)_7L$$

(ix) $$Co(CO)_3L^{\cdot} + Co(CO)_3L^{\cdot} \rightarrow Co_2(CO)_6L_2$$

(x) $$Co(CO)_4^{\cdot} + Co(CO)_4^{\cdot} \rightarrow Co_2(CO)_8$$
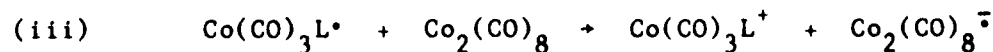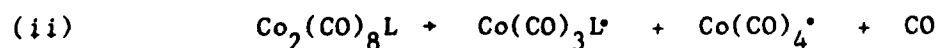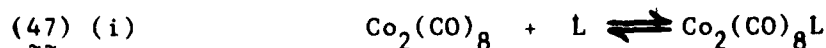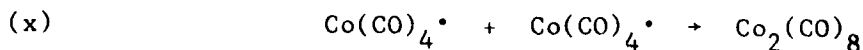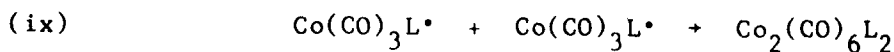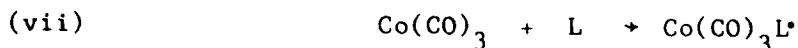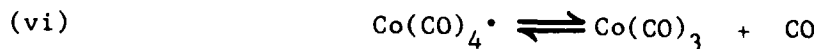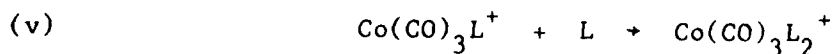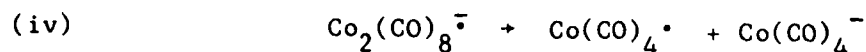
The initial associative step (i) could involve Co–Co bond cleavage of the type noted in 3.1.2 to give a carbonyl bridged dimer of the form $(CO)_3LCo(\mu_2-CO)_2Co(CO)_3$ or $(CO)_4LCo(\mu-CO)Co(CO)_3$, which then could dissociate to two cobalt radical species, $Co(CO)_3L$ and $Co(CO)_4$, with loss of CO. Reaction (iii) involves electron transfer to generate $Co_2(CO)_8^{\overline{\cdot}}$ which, having an electron in its σ^* Co–Co anti-bonding molecular orbital, would be expected to cleave very rapidly.

Evidence for the photoinduced homolysis of metal–metal "two electron" σ-bonds in dinuclear complexes is particularly strong and is well illustrated by the work of Wrighton et al. on the compounds $Cp_2M_2(CO)_6$ (M = Mo, W) (108), $M_2(CO)_{10}$ (M = Mn, Re) (109) and $Co_2(CO)_6(PR_3)_2$ (110).

Strong evidence for the homolysis of the metal–metal bond comes from the isolation of cross-over products upon flash photolysis of mixtures of dinuclear compounds, e.g. reaction 48.

(48) $$Mn_2(CO)_{10} + Re_2(CO)_{10} \xrightarrow{h\nu} MnRe(CO)_{10}$$
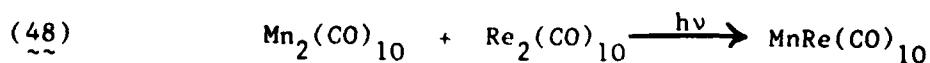
In the case of the compounds $Cp_2M_2(CO)_6$ (M = Mo, W), intense absorption in the UV-visible region of the spectrum has been assigned to the $\sigma_b \rightarrow \sigma^*$ transition of the metal-metal bond (360 nm, M = W; 387 nm, M = Mo). Irradiation causes homolysis of the M-M bond and generation of $Cp_2M_2(CO)_4$ (M≡M) by a mechanism similar to that found upon thermolysis (40,94). In the presence of CCl_4 or Cl_2, the $CpM(CO)_3Cl$ compounds are formed.

Irradiation of these dimers in the presence of ligands such as PPh_3 leads to substitution. The 17 electron radicals generated by homolysis have clearly been shown to be substitutionally labile, probably by initial rapid loss of CO to generate a highly reactive 15 electron species (111), e.g. as in 49.

$$Mn_2(CO)_{10} \underset{}{\overset{h\nu}{\rightleftharpoons}} 2Mn(CO)_5$$

(49) $\quad\quad Mn(CO)_5 + PPh_3 \rightarrow Mn(CO)_4(PPh_3) + CO$

$$2Mn(CO)_4(PPh_3) \rightarrow Mn_2(CO)_8(PPh_3)_2$$
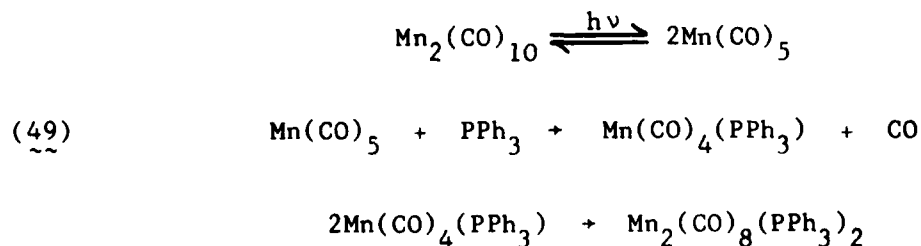
The presence of bridging groups might be expected to reduce the quantum efficiency for the cleavage of metal-metal bonds, since the bridging ligands would hinder separation of the 17 electron species. However, carbonyl bridges do not appear very effective in suppressing photolytic cleavage. Photolysis of $Cp_2Fe_2(CO)_4$ proceeds cleanly to form $CpFe(CO)_2$ and in cross-over experiments involving $M_2(CO)_{10}$ compounds (M = Mn, Re), the heteronuclear products $CpFe(CO)_2M(CO)_5$ are formed (112).

To date, there is no evidence for thermal or photoinduced homolysis of multiple metal–metal bonds in dinuclear systems. Gray et al. (113) noted that photolysis of $[(Bu^n)_4N]_2[Re_2Cl_8]$ in CH_3CN led to formation of mononuclear rhenium containing products, principally $ReCl_3(CH_3CN)_3$. However, it is clear that though this represents a photo assisted cleavage of the Re≡Re bond, a simple photoinduced homolysis is not occuring.

Photoinduced fragmentation of polynuclear metal carbonyl compounds has been observed. For example, the mononuclear $M(CO)_5$ species are formed upon irradiation of $M_3(CO)_{12}$ compounds (M = Fe, Ru) in the presence of CO (114). Similarly, photolysis of $Ru_3(CO)_{12}$ in the presence of PPh_3 leads to mononuclear products, whereas the thermal reaction results only in substitution products. See 50.

$$Ru_3(CO)_{12} \xrightarrow[PPh_3]{\Delta} Ru_3(CO)_9(PPh_3)_3$$

(50)

$$Ru_3(CO)_{12} \xrightarrow[PPh_3]{h\nu} Ru(CO)_4(PPh_3) + Ru(CO)_3(PPh_3)_2$$
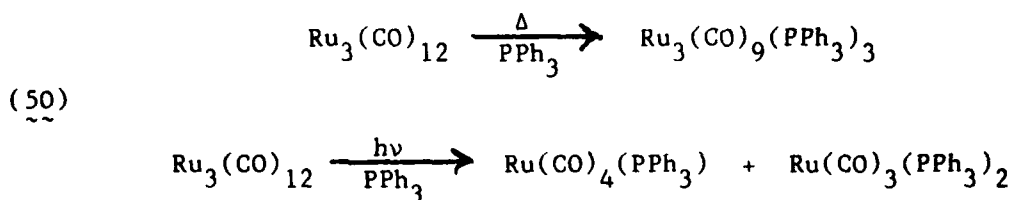
On the basis of a rather limited basis set, it seems that the quantum efficiency for photolytic cleavage of clusters is much lower than that for dinuclear carbonyl compounds. Presumably for a cluster, the cleavage of only one metal–metal bond is less likely to lead to mononuclear fragments and the back reaction, which reforms the cluster, becomes more favorable. This "cluster effect" is seen even for triangulo compounds. Thus, while $Os_3(CO)_{12}$ leads to negligible metal–metal bond rupture upon photolysis (substitution reactions are favored), the carbonyl halide $Os_3(CO)_{10}Cl_2$, which has only two Os–Os bonds, is cleaved much more efficiently (115).

3.1.2. By Ligand Association Reactions with No Formal Oxidation State Change of the Metal

3.1.2.1. By σ-Donor Ligands

The addition of σ-donor ligands to compounds containing metal-metal bonds can lead to cleavage of the M-M bond and formation of mononuclear compounds, e.g. as in 51. These reactions are merely the microscopic reverse of reactions leading to metal-metal bond formation which proceed via initial ligand dissociation. See Section 2.1.2. However, the reactions are sometimes complicated by accompanying electron transfer reactions, leading to products which may be viewed as arising from heterolytic cleavage. Thus, the reaction between $Fe_2(CO)_9$ and excess pyridine yields $[Fe(py)_6]^{2+}[Fe(CO)_4]^{2-}$ (116). This type of cleavage has already been noted in the reaction between $Co_2(CO)_8$ and PR_3 (R = Ph or Bu), reaction sequence 47.

(51) $Fe_2(CO)_9 + PR_3 \rightarrow Fe(CO)_4PR_3 + Fe(CO)_5$
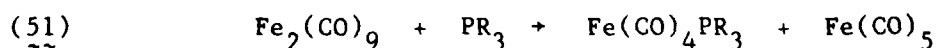
For early transition metal dinuclear complexes containing metal-metal multiple bonds, there are some examples of where the addition of σ-donor ligands ruptures the M-M bond. Undoubtedly, the driving force here is the favorable energetics of sacrificing relatively weak M-M bonds for much stronger M-L σ bonds. This is clearly demonstrated in the reactivity of the $M_2Cl_9^{3-}$ ions with pyridine (M = Cr, Mo, W). On the basis of magnetic and structural considerations, it is well recognized (117) that for M = Cr there is no metal-metal bond, while for M = W, there is a formal triple bond. Addition of pyridine to $Cr_2Cl_9^{3-}$ readily generates mer-$CrCl_3(py)_3$, but the analogous reaction with $W_2Cl_9^{3-}$ yields

$W_2Cl_6(py)_4$ with retention of a strong metal—metal bond (118,119). The related reaction involving $Mo_2Cl_9^{3-}$ and pyridine yields mer-$MoCl_3(py)_3$, but only at $200°C$ (120). In a similar reaction involving $Mo_2(\mu-H)Cl_8^{3-}$ (M≡M) and py, mer-$MoCl_3(py)_3$ was also isolated in 60-70% yield based on Mo, but the cleavage cannot be straight forward since $Mo_2Cl_4(py)_4$ (M≡M) was also isolated.

Two clear-cut examples of the cleavage of metal—metal multiple bonds by σ-donor ligands are shown in reactions 52 (18) and 53 (121).

(52)

X = NCS

(53)

X = Cl
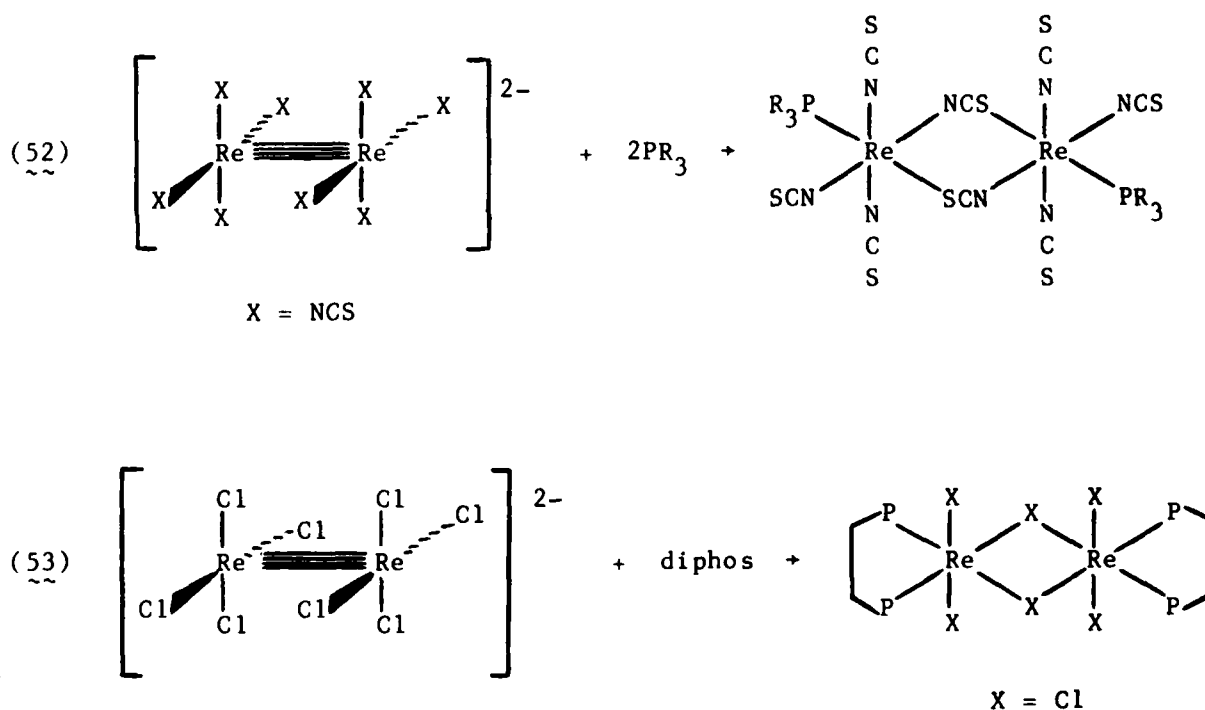
Reactions 52 and 53 transform d^4-d^4 unbridged M-M quadruply bonded dimers to d^4-d^4 high-spin, M-M non-bonded dimers (20). With the ligand bis(diphenylphosphino)methane, dppm, which has a smaller bite and favors bridging two metals (see 2.8), the compound $Re_2Cl_6(dppm)_2$ is formed. On

the basis of spectroscopic data and its diamagnetic nature, the structure shown in XXVI has been proposed. This is the third and intermediate M-M bonding possibility for d^4-d^4 M_2L_{10} dimers.

XXVI
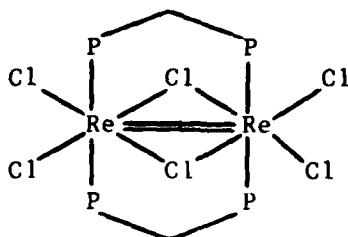
3.1.2.2. By Addition of π-Acceptor Ligands

Early transition metal complexes with M-M multiple bonds seem particularly prone to cleavage by reactions with π-acceptor ligands such as CO, NO and isonitriles RNC. Their effectiveness in these reactions presumably arises from their combined σ donor, π-acceptor properties which allow them to compete for metal atomic orbitals which are otherwise used in forming M-M σ, π and δ bonds. This principle is well illustrated by the clean, quantitative cleavage of the M-M triple bonds by nitric oxide in reactions 54 (122) and 55 (123).

(54)
$$Cp_2M_2(CO)_4 \ + \ 2NO \ \rightarrow \ 2CpM(CO)_2NO$$
$$M = Mo, W$$

(55)
$$Mo_2(OPr^i)_6 \ + \ 2NO \ \rightarrow \ [Mo(OPr^i)_3NO]_2$$
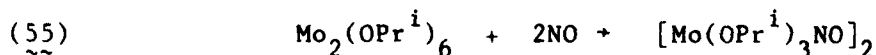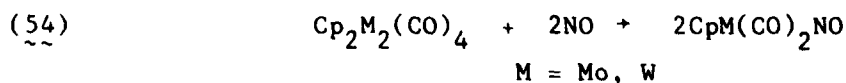
In a formal sense, these reactions correspond to the replacement of the M≡M bond by two Mo≡N-O bonds. The σ electron pair and the two π electron pairs shared by the two metal atoms are redistributed to two σ electron pairs and four π electron pairs in forming two M-NO bonds. The exceedingly low values of ν(NO), ca. 1630 cm^{-1}, together with short M-N

and long N-O distances indicate the multiple nature of the M-N bonds. That the Mo≡Mo bond in $Mo_2(OPr^i)_6$ has been completely cleaved is evident from the Mo-to-Mo distance in $[Mo(OPr^i)_3(NO)]_2$, 3.334(2) Å. Furthermore, the dimeric structure shown in XXVII is readily cleaved by donor ligands to give monomeric compounds of formula $Mo(OPr^i)_3(NO)L$.

XXVII
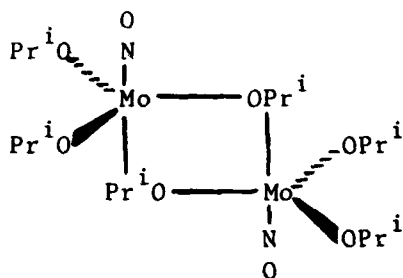
From the reaction between $W_2(OBu^t)_6$ (M≡M) and NO in the presence of pyridine, the mononuclear trigonal bipyramidal molecule $W(OBu^t)_3(NO)(py)$ XXVIII, has been isolated and structurally characterized (124).

XXVIII
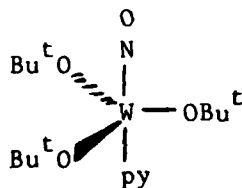
The addition of NO to dichloromethane solutions of $Mo_2X_4L_4$ (M≡M) where X = Cl or Br and L = $PEtPh_2$, PEt_3 or PBu^n_3, and $Mo_2X_4(LL)_2$, where X = Cl or NCS and LL = $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2), gives the 18 electron dinitrosyl monomers $Mo(NO)_2X_2L_2$ and $Mo(NO)_2X_2(LL)$ (125).

Walton and the Boilermakers (126,127) have shown that the M-M triple bond $(\sigma^2\pi^4\delta^2\delta^{*2})$ in $Re_2X_4(PR_3)_4$ compounds (X = Cl or Br; R = Et or

Pr^n) is cleaved by carbon monoxide in refluxing ethanol, toluene or acetonitrile to give the novel paramagnetic 17 electron monomers $ReX_2(CO)_2(PR_3)_2$ which are assigned the <u>trans</u>-geometry XXIX on the basis of spectroscopic data.

XXIX

$$\begin{array}{c} O \\ \| \\ C \\ PR_3 \diagdown \; | \; \diagup X \\ Re \\ X \diagup \; | \; \diagdown PR_3 \\ C \\ \| \\ O \end{array}$$
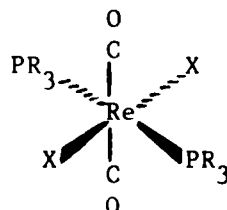
The Mo≡Mo bond ($\sigma^2\pi^4$) in $Mo_2(OR)_6$ compounds (R = Bu^t, Pr^i, Me_3CCH_2) is also cleaved under very mild conditions (1 Atmos, 20^0 C) by the addition of CO. This reaction involves disproportionation as is shown in <u>56</u> (128). The initial step involves the reversible formation of $Mo_2(OBu^t)_6$-(μ-CO) (M≡M).

(<u>56</u>) $\qquad 2Mo_2(OBu^t)_6 + 6CO \rightarrow Mo(CO)_6 + 3Mo(OBu^t)_4$
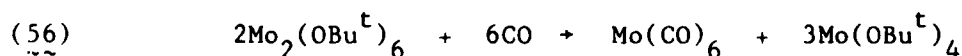
Another example of cleavage involving disproportionation is seen in the reaction between $Mo_2(OPr^i)_6$ and 2,2'-bipyridine, bpy, which yields $Mo(bpy)_2(OPr^i)_2$ and $Mo_2(OPr^i)_8$ (129).

No reaction between CO and M-M quadruply bonded compounds has been found under mild conditions. However, M-M quadruply bonded compounds of the group 6 transition elements containing a central M_2^{4+} unit are all cleaved by isonitriles. Phenylisonitrile reacts to give $M(CNPh)_6$ compounds (M = Cr, Mo, W). It is not known whether this represents a disproportionation product or whether there are oxidized organic products. In the presence of non-coordinating anions, such as PF_6^-, addition

of alkylisonitriles to $Mo_2(OAc)_4$ or $Mo_2Cl_8{}^{4-}$ gives $Mo(CNR)_7{}^{2+}(PF_6{}^-)_2$ salts. The related W-W quadruply bonded acetate and octachloro salts are not known, but Walton has shown that addition of RNC (R = Bu^t or cyclo-C_6H_{11}) and KPF_6 to an acetone solution of $W_2(mhp)_4$ (M$\equiv$M) (mhp = the anion of 2-hydroxy-6-methylpyridine) yields the homoleptic isonitrile complexes $W(CNR)_7{}^{2+}(PF_6{}^-)_2$ upon heating (130). Addition of RNC to Mo_2Cl_4-$(PR'_3)_4$ and $Mo_2Cl_4(dppe)_2$ in the presence of KPF_6 leads to the mixed isonitrile phosphine cations $Mo(CNR)_6(PR'_3)^{2+}$ and $Mo(CNR)_5(dppe)^{2+}$, respectively.

The quadruple M-M bond in Re(3+) dimers is also cleaved by alkyl isonitriles. Treatment of $Re_2(OAc)_4Cl_2$ with neat Bu^tNC is reported (131) to give $ReCl(CNBu^t)_5$ in 80% yield, while when such a reaction is carried out in refluxing MeOH in the presence of KPF_6, $Re(CNBu^t)_6{}^+PF_6{}^-$ may be obtained in 60% yield (130).

Carbon monoxide and isonitriles are also well known to cleave metal-metal single bonds. This is presumably the reaction that occurs in the formation of $M(CO)_5$ (M = Fe, Ru, Os) from $Fe_2(CO)_9$ or $M_3(CO)_{12}$ and CO under high pressure. The vigorous conditions imply that attack on these saturated systems is slow. By contrast, the compounds $Os_3(\mu-H)_2(CO)_{10}$ and $Mo_2(OBu^t)_6$, which contain M-M double and triple bonds, respectively, react rapidly and reversibly with CO at room temperature. These reactions are discussed further in Section 3.2. The direct attack on a single bond presumably proceeds to give a bridged non-M-M bonded intermediate, which then breaks apart, 57.

$$M-M \ + \ X \ \rightarrow \ M \overset{X}{\diagdown} M$$

(57)

$$M \overset{X}{\diagup} M \ \rightarrow \ M-X \ + \ M \xrightarrow{+X} \ 2M-X$$
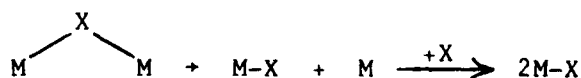
In the presence of the bridging ligands, dam $(Ph_2AsCH_2AsPh_2)$ and dppm $(Ph_2PCH_2PPh_2)$, carbonyl (132) and isonitrile bridged (133) non-M-M bonded dimers have been isolated and structurally characterized from reaction 58. Cleavage of the Pd-Pd bond is accompanied by an increase in the Pd-Pd distance of ca. 0.6 Å. Reaction 58 is reversible for CO, but not for RNC.

(58)

$$Cl-Pd-Pd-Cl \xrightarrow{+X}$$

[X = CO, Y = Ph_2As; X = RNC, Y = Ph_2P]
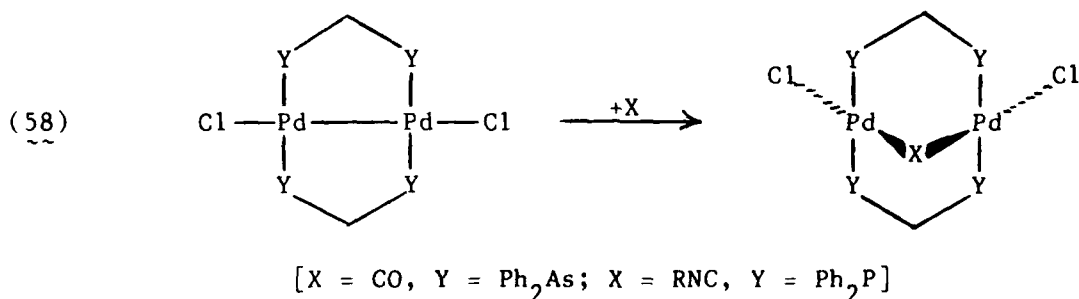
3.1.3. By Oxidative-Addition Reactions

A large number of mononuclear metal carbonyl halides and hydrides are formed by the addition of X_2 (X = Cl, Br, I) or H_2 across a metal-metal bond. A classic example (134) is seen in the bromination of dimanganesedecacarbonyl, 59. The mechanism of addition may involve initial homolysis of the M-M bond (Section 3.1.1), loss of a CO ligand or possibly electron transfer. The resulting metal carbonyl halide may undergo CO loss and association by halide bridge formation, 60. Similar metal-metal bond cleavage and bridge formation is often seen in reactions

of R_2PX with dinuclear and polynuclear carbonyls, e.g. as in reaction 61 (135).

(59) $\qquad Mn_2(CO)_{10} + Br_2 \xrightarrow{40^{\circ}C} 2Mn(CO)_5Br$

(60) $\qquad 2Mn(CO)_5Br \xrightarrow{\Delta} Mn_2(CO)_8(\mu-Br)_2$

(61) $\qquad Mn_2(CO)_{10} + (CF_3)_2PI \rightarrow Mn_2(CO)_8(\mu-P(CF_3)_2)(\mu-I)$
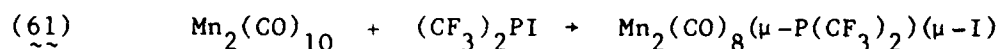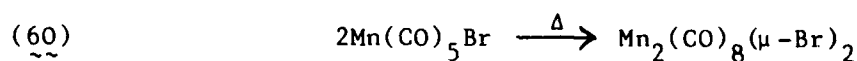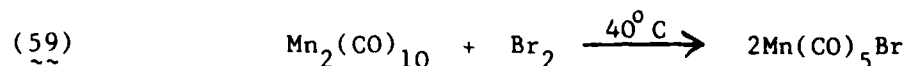
A similar reaction between $Os_3(CO)_{12}$ and Cl_2 leads to cleavage of one of the metal-metal bonds and an opening of the triangulo structure. Upon heating, CO is lost and a cyclic product is formed having two Os-Os bonds and a pair of bridging chlorides spanning the non-bonded osmium atoms, 62 (136).

(62)

$Os_3(CO)_{12}$ + Cl_2 → $Os_3(CO)_{12}Cl_2$ $\xrightarrow[-2CO]{\Delta}$ $Os_3(CO)_{10}Cl_2$
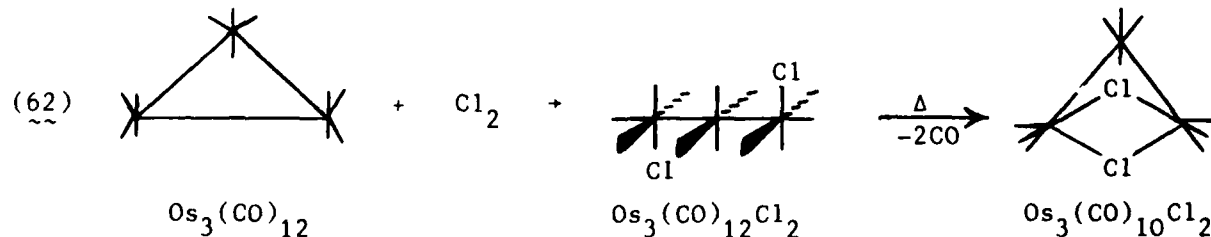
The introduction of halides or other potentially 3 electron donor groups by addition reactions causes problems in predicting the metal-metal bond order of the products. For example, addition of I_2 to Cp_2Mo_2-$(CO)_4$ (M≡M) gives a diamagnetic dimeric product of formula $Cp_2Mo_2(CO)_4I_2$ which could either exist as an unbridged compound with a Mo=Mo bond or as a diiodobridged molecule with no metal-metal bond (137). In fact, the compound does exist in two isomeric forms and the structure of one isomer in the solid state is shown in Figure 3.1. The diiodobridge structure has

48

Figure 3.1. An ORTEP view of the $Cp_2Mo_2(CO)_4I_2$ molecule.
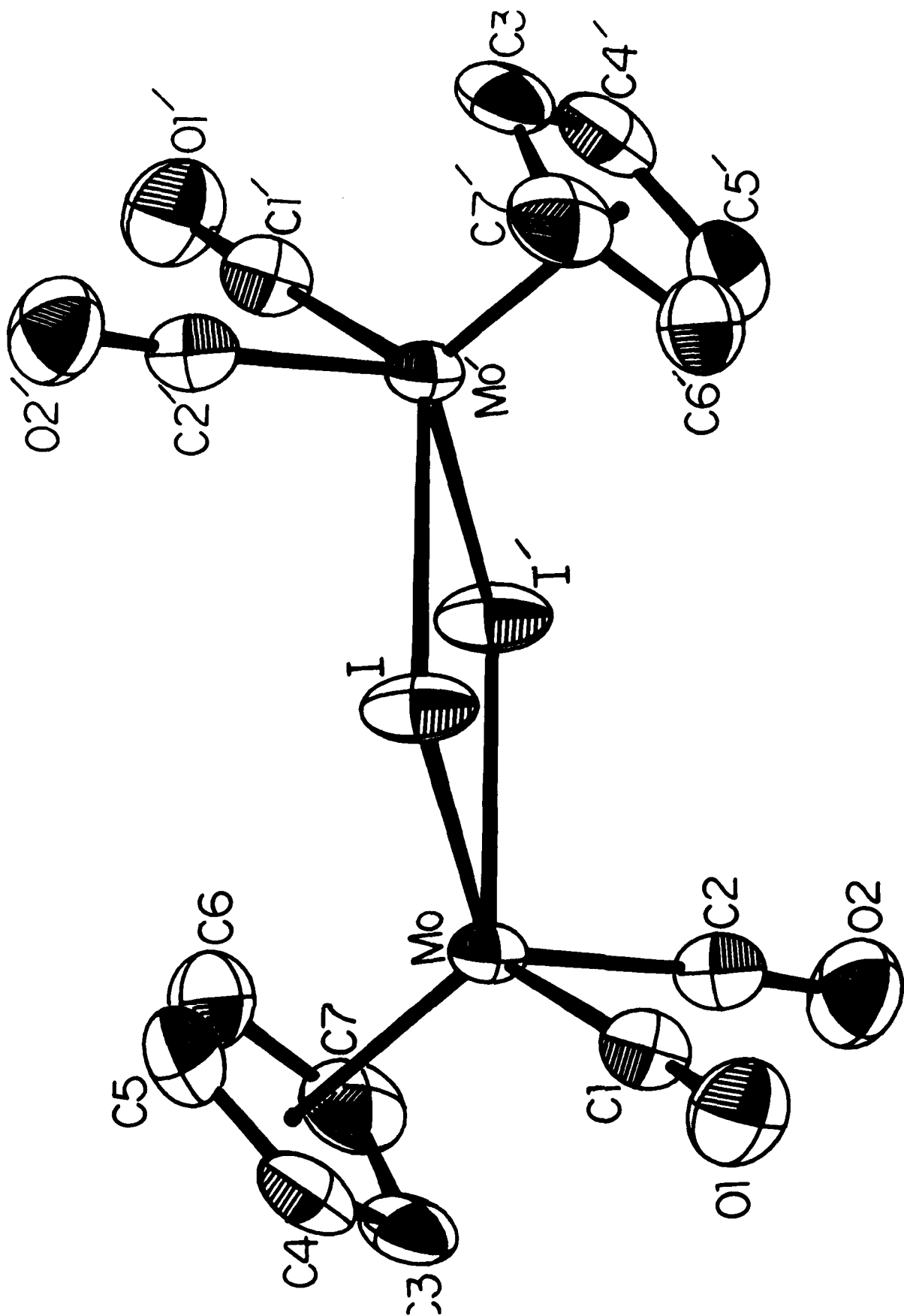
a Mo-to-Mo distance of 4.41 Å, indicative of the absence of any Mo-Mo bond. Thus, by the combined reactions of oxidative addition and Lewis base association, addition of I_2 to $Cp_2Mo_2(CO)_4$ cleaves the Mo≡Mo bond. It is, however, relatively rare to cleave a metal-metal multiple bond by a single oxidative addition reaction and few examples come to mind. The Mo=Mo bond in $Mo_2(OPr^i)_8$ is cleaved by the addition of molecular oxygen, 63 (138). Here, a metal-metal double bond is replaced by a metal-oxygen double bond. The Mo-Mo triple bond in $Mo_2(OBu^t)_6$ is also cleaved by O_2 and aryl azides, reactions 64 and 65, but these require more than one equivalent of the oxidizing substrates and must occur in stepwise processes (139).

(63) $Mo_2(OPr^i)_8$ (M=M) + O_2 → $2MoO(OPr^i)_4$

(64) $Mo_2(OBu^t)_6$ + $2O_2$ → $2MoO_2(OBu^t)_2$ + $2Bu^tO\cdot$

(65) $Mo_2(OBu^t)_6$ + $4ArN_3$ → $4N_2$ + $2Bu^tO\cdot$ + $[Mo(OBu^t)_2(NAr)(\mu-NAr)]_2$
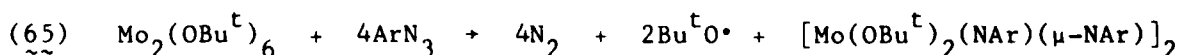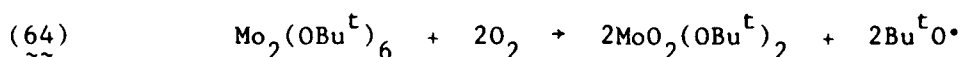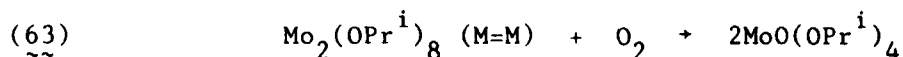
3.1.4. By Reduction Reactions

The only common example involves the reduction of dinuclear or polynuclear metal carbonyl compounds by electropositive metals or alloys, typically sodium or sodium amalgam. Three well known examples are shown in 66 (140), 67 (141) and 68 (142). Also, the cyclopentadienyl metal carbonyl anions, $CpNi(CO)^-$, $CpFe(CO)_2^-$ and $CpMo(CO)_3^-$, are readily made by addition of alkali metals to tetrahydrofuran solutions of $Cp_2Ni_2(CO)_2$, $Cp_2Fe_2(CO)_4$ and $Cp_2Mo_2(CO)_6$, respectively (143).

(66) $Fe_3(CO)_{12}$ + 6Na → $3Na_2[Fe(CO)_4]$

(67) $$Co_2(CO)_8 + 2Na \rightarrow 2Na[Co(CO)_4]$$

(68) $$Mn_2(CO)_{10} + 2Na \rightarrow 2Na[Mn(CO)_5]$$
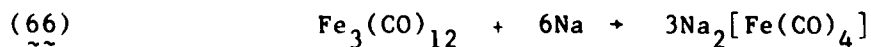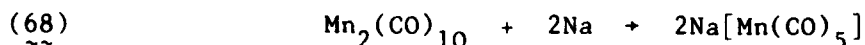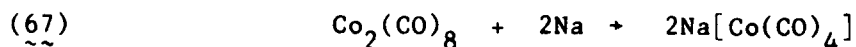
3.2. Without Cleavage of Metal-Metal Bonds

3.2.1. By Addition Reactions

Addition reactions to dinuclear compounds can lead to bond order reductions which, without cleavage, can take the form $4 \rightarrow 3$, $4 \rightarrow 2$, $4 \rightarrow 1$; $3 \rightarrow 2$, $3 \rightarrow 1$ and $2 \rightarrow 1$. Furthermore in some cases, addition reactions can lead to increases in M-M bond order if electrons are removed from anti bonding M-M molecular orbitals. There are also a few reactions which lead to fractional (one-half for dinuclear compounds) bond order changes. For cluster compounds, the changes in molecular orbital configuration can lead to delocalized changes over the M_n skeleton or may result in specific changes within localized M-M bonds. At this time, not all the possible transformations have been experimentally documented.

3.2.1.1. Bond Order Changes from 4 to 3

Bonds of order 4 are unique to compounds of the early transition elements, specifically the d^4-d^4 dimers Cr_2^{4+}, Mo_2^{4+}, W_2^{4+} and Re_2^{6+}. Examples of the reduction in bond order from 4 to 3 are rare. The best documented example involves the reaction between $Mo_2(OAc)_4$ and aqueous solutions of HX (X = Cl, Br). The initial reaction produces $Mo_2X_8^{4-}$, with retention of the quadruple bond, but at $+60^\circ C$, the $Mo_2X_8H^{3-}$ ion is formed (144). The structure of the anion, XXX, is analogous to that of $Mo_2Cl_9^{3-}$ (145). The formation of $Mo_2X_8H^{3-}$ anion can be viewed as oxidative addition of HX across the Mo-Mo quadruple bond.

3-

XXX

$$Mo \equiv Mo$$
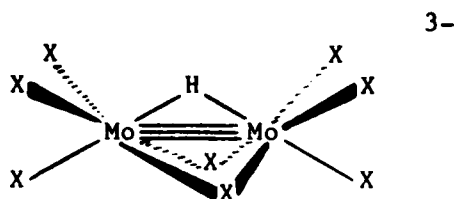
3.2.1.2. <u>Bond Order Changes from 4 to 2</u>

Probably the only known example involves the addition of bisdiphenylphosphinomethane, dppm, to $Re_2Cl_8{}^{2-}$ which gives $Re_2Cl_6(dppm)_2$ (see XXVI, Section 3.1.2). Based on spectroscopic and magnetic data, this compound is formulated as a Vahrenkamp d^4-d^4 M_2L_{10} compound with a metal-to-metal double bond (20).

3.2.1.3. <u>Bond Order Changes from 4 to 1</u>

An interesting, and at this time perhaps the only, example of this transformation is seen in the reactions between the xanthate $Mo_2(S_2COEt)_4$ and the halogens X_2 (X = Br, I) which yield $Mo_2X_2(S_2COEt)_4$ compounds. The structural analyses (146) showed that these compounds did not contain $Mo\equiv Mo$ bonds as might have been expected, but rather single bonds with Mo–Mo distances of 2.72 Å (averaged). This results from a surprising rearrangement of the xanthate ligands as is shown in Figure 3.2. Two of the xanthate ligands act as 4 electron π-donors across the Mo-Mo bond. In this way, each molybdenum atom attains an 18 valence shell of electrons by forming a Mo–Mo single bond.

3.2.1.4. <u>Bond Order Changes from 3 to 2</u>

A number of examples of changes in metal–metal bond order from 3 to 2 have recently been found in the chemistry of $M_2(OR)_6$ compounds (M = Mo, W). Addition of CO leads to disproportionation products with cleavage of

Figure 3.2. An ORTEP view of the $Mo_2(S_2COEt)_4I_2$ molecule showing the unusual bridging xanthate ligands.
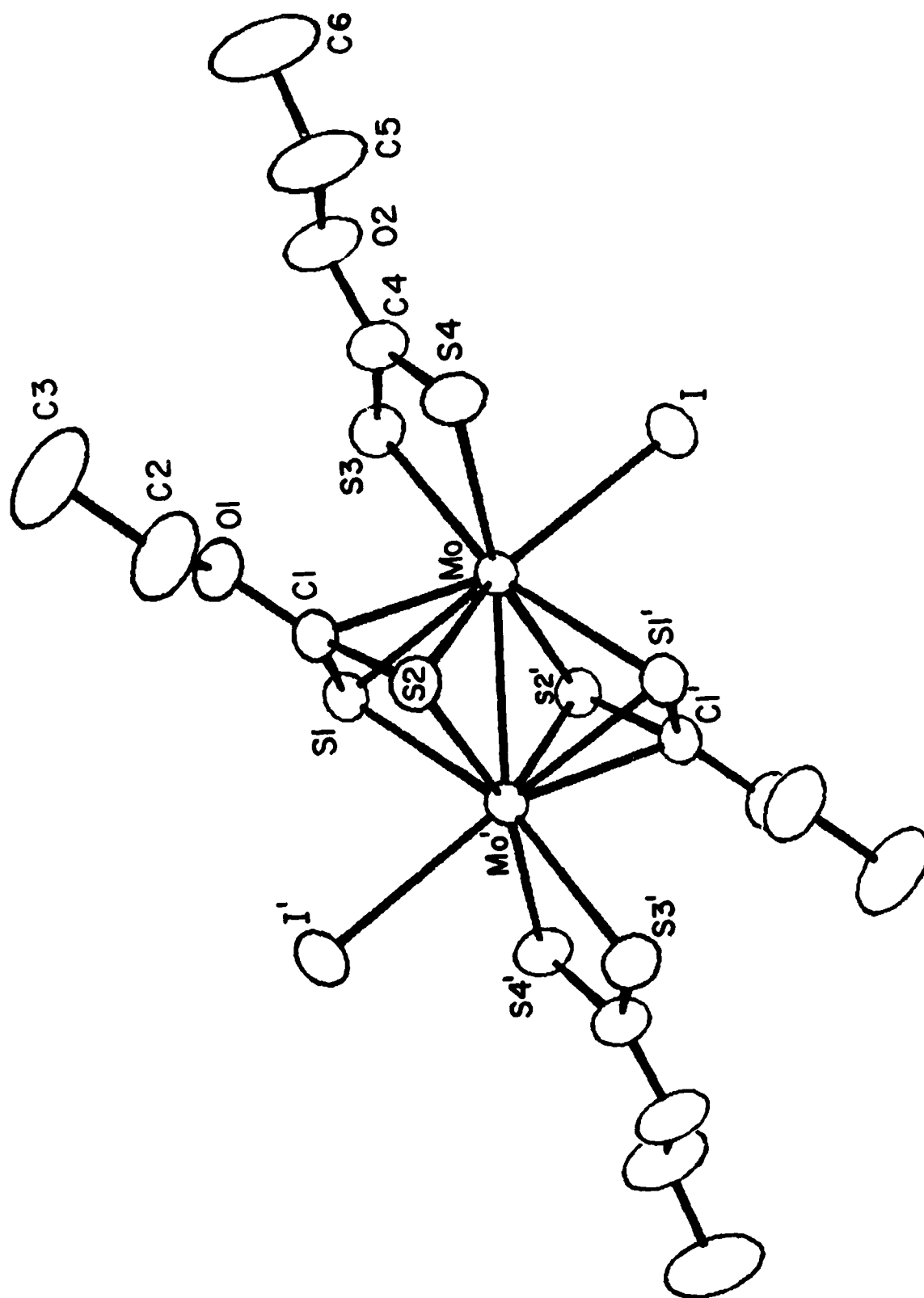
the M≡M (Section 3.1.2), but for M = Mo and R = Bu^t, an initial reversible addition has been shown to give $Mo_2(OBu^t)_6(\mu-CO)$ (128). See Figure 3.3. The Mo-Mo distance is 2.498(1) Å, which together with simple electron counting is consistent with the presence of a Mo=Mo bond.

Addition of CO to $M_2(OPr^i)_6$ compounds in the presence of pyridine gives closely related $M_2(OPr^i)_6(py)_2(\mu-CO)$ compounds (147). The sixth coordination site of the metal atoms, which is <u>trans</u> to the M-μ-CO bond and is vacant in $Mo_2(OBu^t)_6(\mu-CO)$, is now occupied by a pyridine ligand. Similarly, addition of acetylene to $Mo_2(OPr^i)_6$ in the presence of pyridine generates an adduct $Mo_2(OPr^i)_6(py)_2(\mu-C_2H_2)$. See Figure 3.4. The Mo-Mo distance is 2.55 Å and the C-C distance is 1.38 Å, which are consistent with Mo=Mo and C=C bonds, respectively (148).

Addition of Pr^iOH to $W_2(NMe_2)_6$ in the presence of pyridine gives $W_2(OPr^i)_6(py)_2$ and dimethylamine. In the absence of pyridine, a tetranuclear compound, $W_4(\mu-H)_2(OPr^i)_{14}$, is formed. This may be viewed as the product of oxidative addition of Pr^iO-H across a W≡W bond, 69 (149). An ORTEP view of the central skeleton of this centrosymmetric molecule is shown in Figure 3.5. The W-W distance at each end of the W_4 chain is short (2.44 Å), while the central W-W distance is long (3.4 Å), corresponding to metal-metal double and non-bonding distances, respectively.

(69) $W_2(OPr^i)_6 \; + \; Pr^iOH \; \rightarrow \; \frac{1}{2}[W_2(\mu-H)(OPr^i)_7]_2$
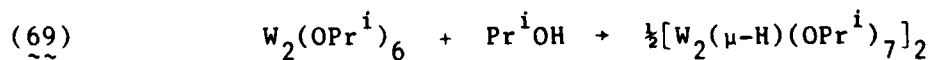
Another example of oxidative addition to a M≡M bond which leads to a M=M bond is seen in reaction 70 (150).

Figure 3.3.   An ORTEP view of the central skeleton of the $Mo_2(OBu^t)_6$-(μ-CO) molecule.
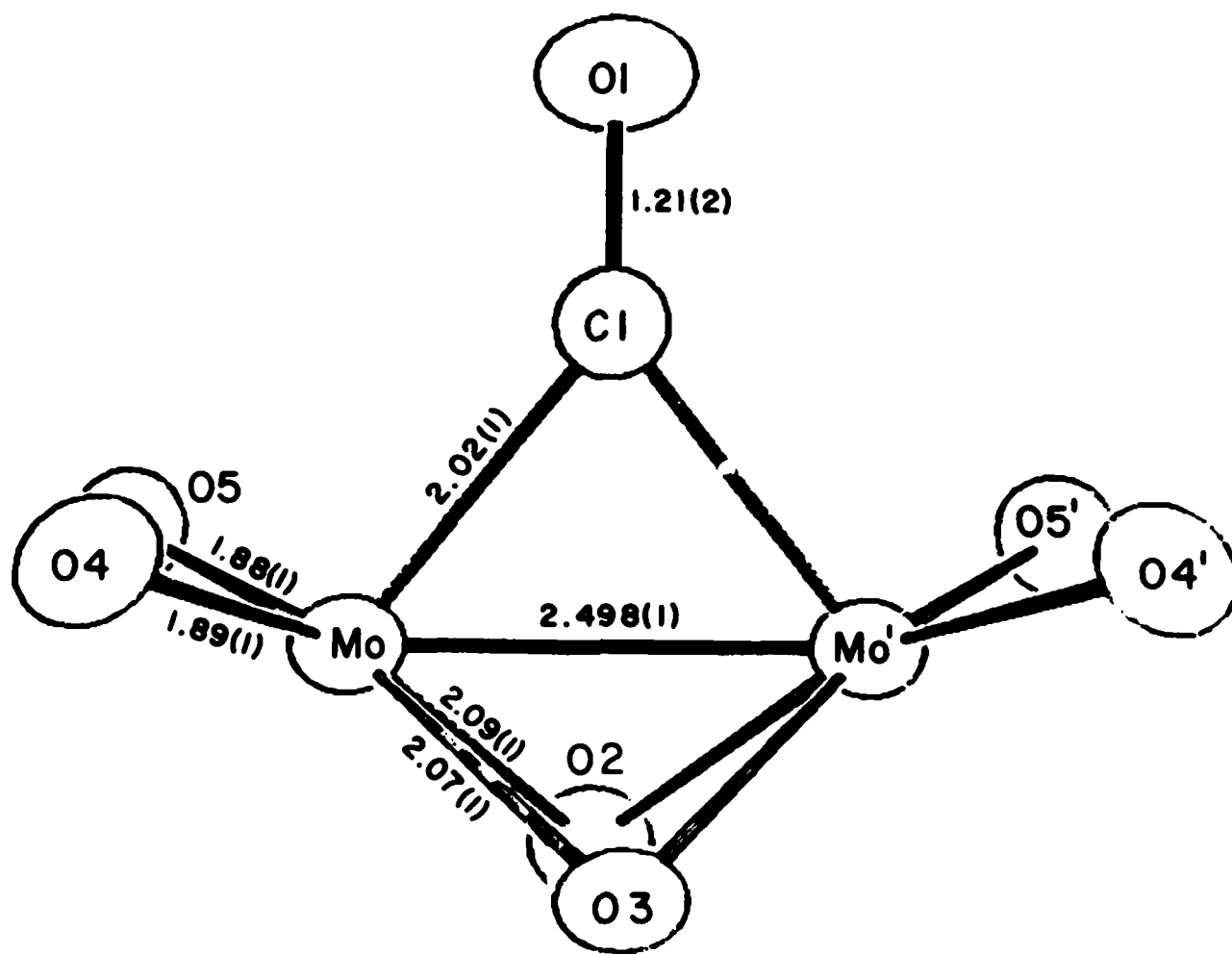
$Mo_2O_6(CO)$ Skeleton of

$Mo_2(O\text{-}t\text{-}Bu)_6(CO)$

Figure 3.4.   An ORTEP view of the central $Mo_2O_6N_2(C_2H_2)$ skeleton of the $Mo_2(OPr^i)_6(py)_2(\mu-C_2H_2)$ molecule.
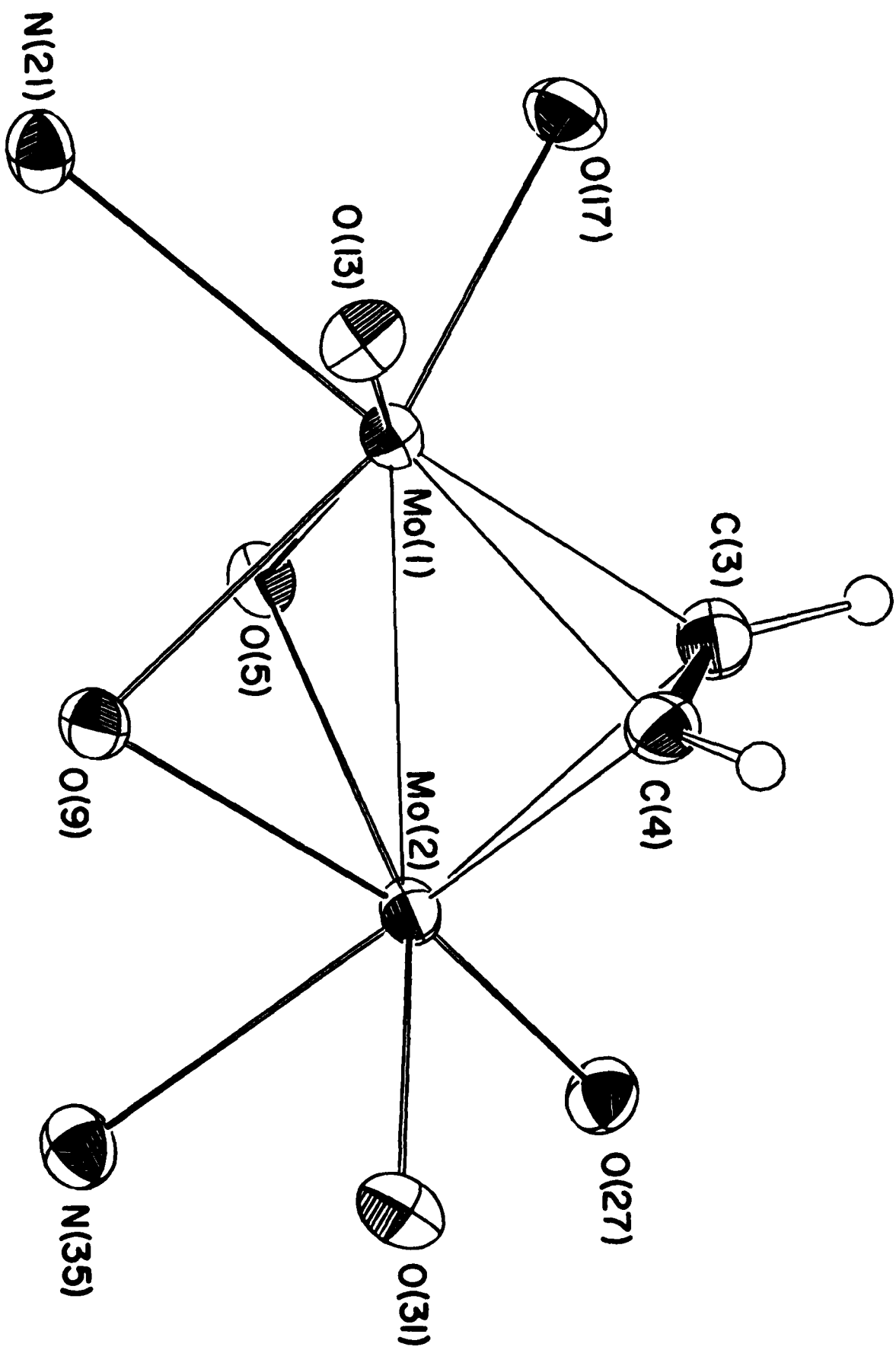
Figure 3.5.   An ORTEP view of the central $W_4(\mu-H)_2O_{14}$ skeleton of the $W_4(H)_2(OPr^i)_{14}$ molecule emphasizing the octahedral coordination of each tungsten atom.

(70) Pr^iO, Pr^iO — $Mo \equiv Mo$ — OPr^i, $-OPr^i$, Pr^iO, OPr^i + Pr^iO-OPr^i → (alkoxide-bridged dimer structure)
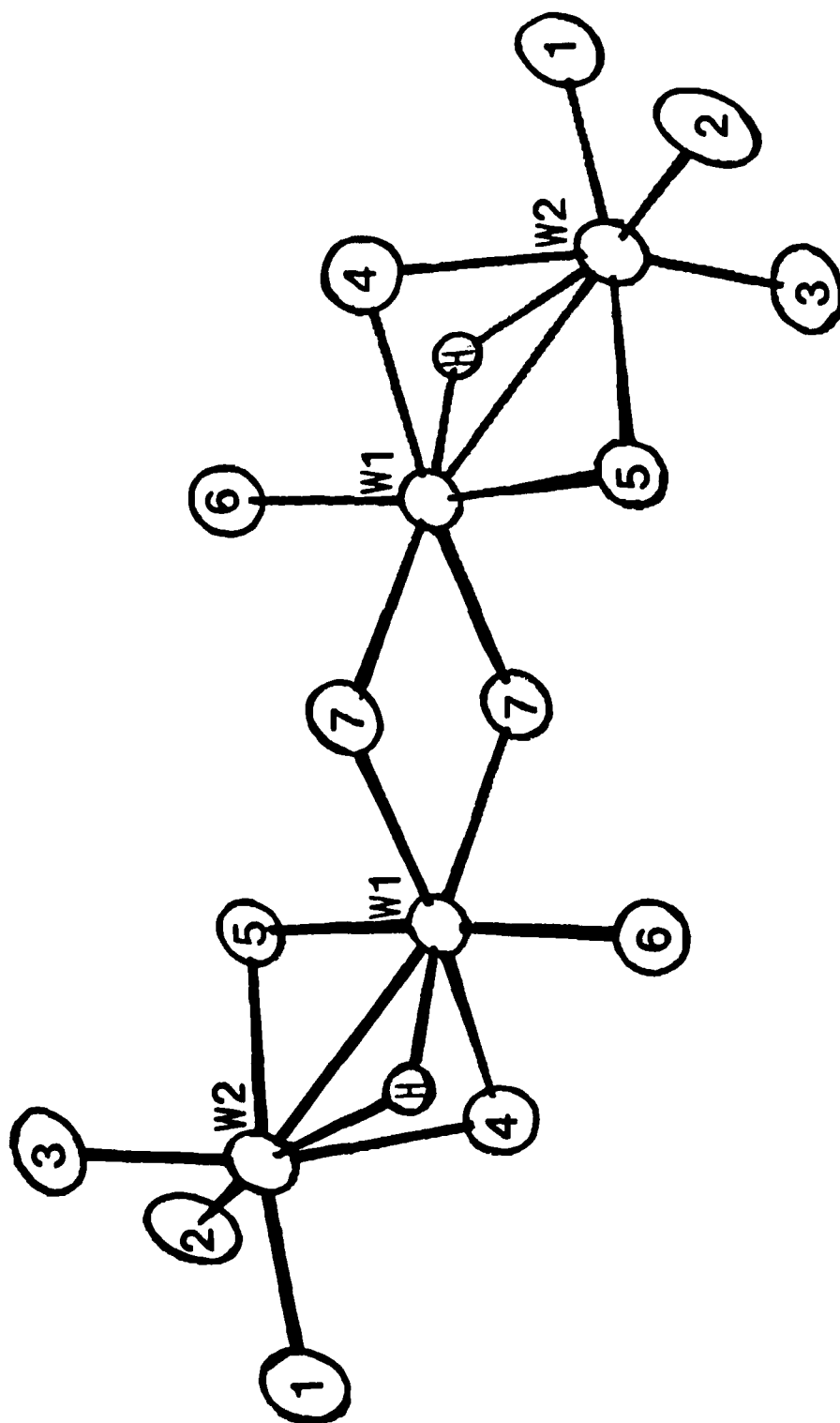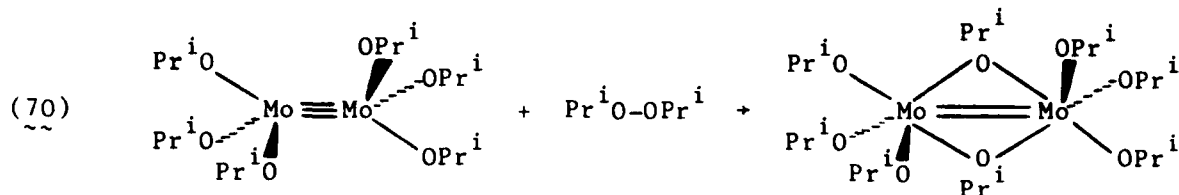
In all of these oxidative addition reactions, alkoxide bridges are formed. This may be understood as an intramolecular Lewis base association reaction which occurs in response to the increased Lewis acidity of the metal atoms upon oxidation.

3.2.1.5. Bond Order Changes from 3 to 1

Numerous reactions are known in which a metal-to-metal triple bond is transformed to a single bond. These reactions presumably proceed through reactive intermediates with M–M double bonds. For example, addition of X_2 molecules (X = Cl, Br and I) to $Mo_2(OPr^i)_6$ gives $Mo_2(OPr^i)_6X_4$ (M–M) compounds (150). Attempts to isolate intermediate compounds of formula $Mo_2(OPr^i)_6X_2$ were unsuccessful.

The $Cp_2M_2(CO)_4$ (M≡M) compounds (M = Mo, W) undergo a large number of addition reactions, many of which lead to M–M single bonds. The addition of monodentate ligands, L, proceeds to give $Cp_2M_2(CO)_4L_2$ (M–M) compounds when L = $P(OR)_3$, PR_3 and CO (151). Based on simple electron counting considerations, one might expect that the intermediates of formula $Cp_2M_2(CO)_4L$ would have M=M bonds. However, it is quite possible that even in these reactive intermediates, the M=M bond is avoided since one of the carbonyl ligands could act as a four electron donor as shown in XXXI. The addition of CN⁻ leads to $[Cp_2Mo_2(CO)_4(CN)]^-$ in which the CN⁻

ligand acts as a four electron donor in an analogous manner to that shown for CO in XXXI (152).

XXXI
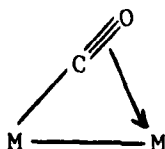
A number of other unsaturated molecules, un, react with $Cp_2Mo_2(CO)_4$ to give $Cp_2Mo_2(CO)_4(un)$ adducts in which the un act as four electron donors and span the two metal atoms, e.g. un = $RC\equiv CR$ (153), allenes (154), $R_2NC\equiv N$ (155) and $R_2C=S$ (156). See Figure 3.6. Addition of diaryl-diazo compounds yield initially 1:1 adducts, XXXII, which upon heating to $60°C$ evolve N_2 to give the carbene bridged adducts XXXIII. In both instances, however, there are Mo—Mo single bonds since the bridging groups act as four electron donors to the Mo_2 center (157).
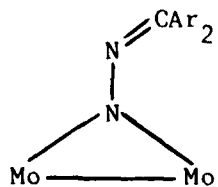
XXXII
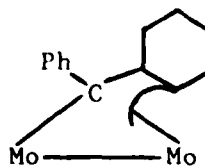
XXXIII

3.2.1.6. Bond Order Changes from 2 to 1

The number of compounds containing metal-metal double bonds is small and, as is seen in Section 3.2.1.5, reactions often proceed to bypass these compounds. By far the most studied compound containing a M=M bond is $Os_3(CO)_{10}(\mu-H)_2$ (158). This compound readily picks up monodentate ligands such as CO to yield an Os-Os single bond, 71 (159).

Figure 3.6. Schematic representations of the $Cp_2Mo_2(CO)_4(un)$ molecules, where un = RCCR, $CH_2=C=CH_2$ and Me_2NCN, showing how the unsaturated molecules span the dimetal center.

(A)

(B)

(C)

(71)

$$\text{(structure: } Os_3(CO) \text{ cluster with bridging H's, M=M bond)} + L \rightarrow \text{(product cluster with L and H)}$$
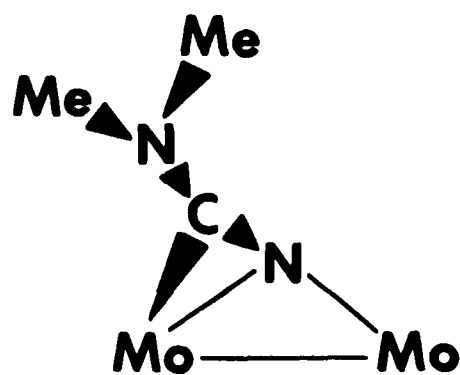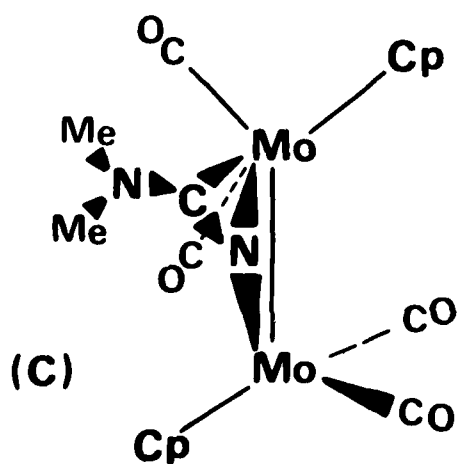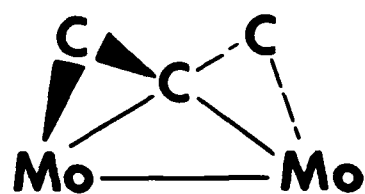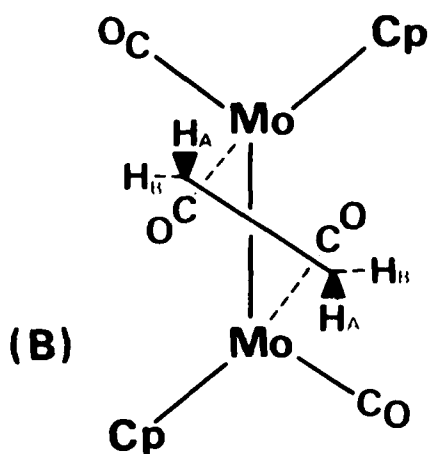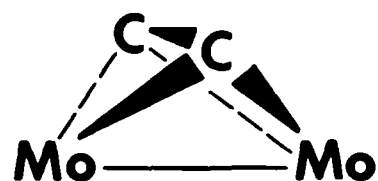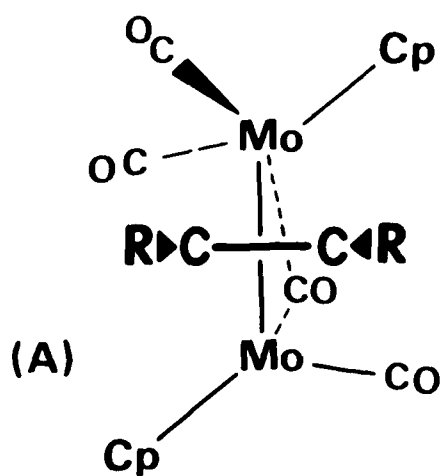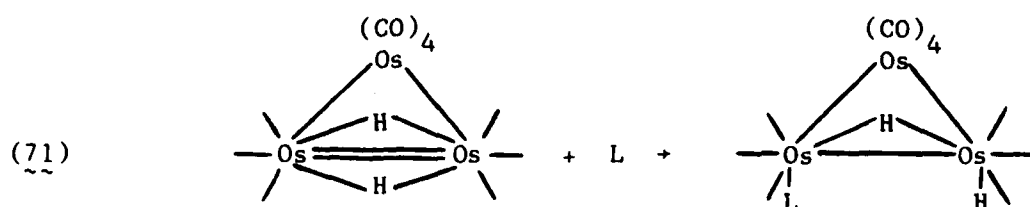
A number of unsaturated molecules, un, react with $Os_3(CO)_{10}(\mu\text{-H})_2$ to yield products of insertion into one of the hydride ligands and generation of a four electron donor bridging ligand un' which spans an Os-Os single bond as shown in 72. These reactions are discussed in Section 4.2.

(72)

$$\text{(structure: } Os_3(CO) \text{ cluster with two bridging H's and M=M bond)} + un \rightarrow \text{(product cluster with bridging un')}$$
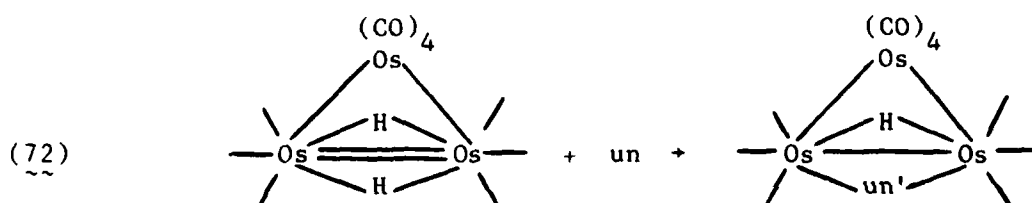
Although other carbonyl hydrides are known with M=M bonds, e.g. $W_2(CO)_8H_2^{2-}$, $H_2Re_2(CO)_8$ and $H_4Re_4(CO)_{12}$, their reactivity is little known. As noted in Section 2.7, addition of a low valent coordinatively unsaturated metal fragment across a M=M bond can generate trinuclear complexes with M-M single bonds. The dinuclear compound $Re_2(CO)_6(dppm)$-$(\mu\text{-H})_2$ has been shown to react with $P(OMe)_3$ to give XXXIV (160), which is analogous to reaction 71.

XXXIV

$$\text{(structure: } Re_2 \text{ complex with dppm bridge, CO ligands, P(OMe}_3\text{), and H)}$$
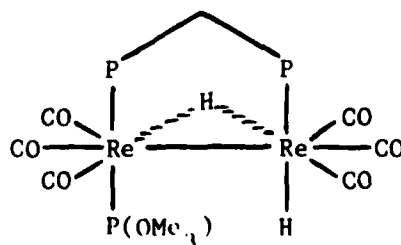
3.2.1.7. Bond Order Changes from 3 to 4

For a dimetal center with an electronic configuration $\sigma^2\pi^4\delta^2\delta^{*2}$, oxidative addition can lead to an increase in M-M bond order from 3 to 4 and this is realized in reaction 73 (161).

$$(73) \qquad Re_2Cl_4(PR_3)_4 \xrightarrow{\;O_2/HCl\;} Re_2Cl_5(PR_3)_3 \xrightarrow{\;O_2HCl\;} Re_2Cl_6(PR_3)_2$$

3.2.1.8. Fractional Bond Order Changes

Reactions involving the oxidation or reduction of the metal ions by an even number of electrons presumably occur in stepwise reactions involving the transference of a single electron. The overall integral change in M-M bond order can be broken down into two reactions involving a half order change. This is clearly the case in reaction 73 where the compounds $Re_2Cl_4(PR_3)_4$, $Re_2Cl_5(PR_3)_3$ and $Re_2Cl_6(PR_3)_2$ have Re-Re bond orders of 3, 3.5 and 4, respectively. Though not common, quite a few reactions are known to lead to compounds with fractional bond orders, e.g. $Mo_2(SO_4)_4{}^{3-}$ (162) and $Cp_2Co_2(CO)_2{}^-$ (163), which have bond orders of 3.5 and 1.5, respectively. A particularly interesting and synthetically useful reaction was discovered by McCarley et al. (164). From the reaction between $Mo(CO)_6$, $W(CO)_6$ and Me_3CCOOH, mixtures of $Mo_2(O_2CCMe_3)_4$ and $MoW(O_2CCMe_3)_4$ were obtained. Addition of I_2 to a benzene solution of a mixture of these Mo_2 and MoW compounds selectively precipitated the heterobimetallic single electron oxidation product $MoW(O_2CCMe_3)_4I$ and a crystal structure of the acetonitrile adduct revealed axial coordination of I^- to W and MeCN to Mo. The compound has a Mo-W bond order of 3.5 and

reduction, using powdered zinc in acetonitrile at $25^{o}C$, yielded the heteronuclear quadruply bonded compound $MoW(O_2CCMe_3)_4$.

Finally, it should be recognized that certain oxidative addition reactions can occur to dinuclear metal centers with no formal change in M-M bond order. This is seen in the addition of HX or X_2 (X = Cl, Br) to the Rh(I)-Rh(I) d^8-d^8 dimers of the type $Rh(bridge)_4^{2+}$ to give d^7-d^7 (Rh(II)-Rh(II)) dimers, $Rh_2(H)(X)(bridge)_4^{2+}$ or $Rh_2X_2(bridge)_4^{2+}$. The metal-metal bond order is formally one in both the d^8-d^8 and d^7-d^7 dimers, though the strength of the bond, as evidenced by metal-metal distances, increases upon oxidation: the Rh-Rh distance descreases with oxidation (165).

3.2.2. By Reductive Elimination Reactions

Whereas most multiple bonds in organic chemistry are made by elimination reactions, relatively few inorganic analogues have been established.

The loss of CO from $H_2Os_3(CO)_{11}$ which occurs on heating in low boiling solvents is just the microscopic reverse of 71 and provides an example of an M-M bond order transformation from one to two.

The acetylene adducts $Cp_2Mo_2(CO)_4(R_2C_2)$ react with H_2 at elevated temperatures to generate cis-olefins and the triply bonded compound $Cp_2Mo_2(CO)_4$. The reaction apparently proceeds via initial loss of CO (166). The sequence thereafter is not known, but it is not unreasonable to suppose that elimination proceeds via a hydrido-vinyl compound of the type shown in XXXV. Bridging vinyl compounds, similar to XXXV, can be generated by protonation of the acetylene adduct (167).

$$\text{XXXV} \qquad (CO)_2CpMo \overset{\overset{\displaystyle CH \!\!=\!\! CH_2}{\diagup\;\;\searrow}}{\underset{\diagdown H \diagup}{\rule{3cm}{0.4pt}}} MoCp(CO)_2$$
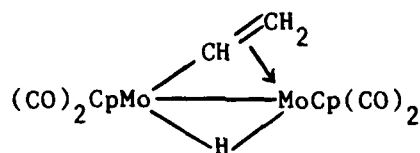
The elimination of CO from $Mo_2(OBu^t)_6(\mu\text{-}CO)$ changes a Mo-Mo double bond to a triple bond (128) and the alkyl group disproportionation reactions 74 and 75 provide examples of where Mo-Mo triple bonds are converted to quadruple bonds (168,169). The presence of β-hydrogens is apparently key in reactions 74 and 75, since when R = Me or CH_2SiMe_3, compounds of formula $Mo_2R_2(O_2CNMe_2)_4$ and $Mo_2R_2(NMe_2)_2(ArN_3Ar)_2$ are obtained in which the Mo≡Mo bonds are retained (170). Reaction 74 involving the labelled compound $Mo_2(CH_2CD_3)_2(NMe_2)_4$ gave only $CH_2 = CD_2$ and CH_2DCD_3. In cross-over experiments, no deuterium was transfered and all available evidence is consistent with an intramolecular reaction pathway. There is a strong analogy between the dialkyl group disproportionation reactions 74 and 75 and thermal decomposition pathways of mononuclear dialkyl metal complexes, such as $L_2Pt(n\text{-}Bu)_2$ which gives $L_2Pt(0)$ and 1-butene and butane (171). However, while the β-hydrogen elimination process at a mononuclear center proceeds via a four membered transition state, XXXVI, a dinuclear complex may react via a five-membered transition state, XXXVII, involving both metal atoms. The detailed pathway by which alkane is formed in 74, and 75 is not yet known.

(74) $1,2\text{-}Mo_2R_2(NMe_2)_4 + CO_2$ (excess) →

$$Mo_2(O_2CNMe_2)_4 + \text{alkane} + \text{alkene}$$

[R = Et, i-Pr, n-Bu, t-Bu]

(75) $1,2\text{-}Mo_2R_2(NMe_2)_4$ + ArNNNHAr (excess)   →

$Mo_2(ArN_3Ar)_4$ + $4HNMe_2$ + alkane + 1-alkene
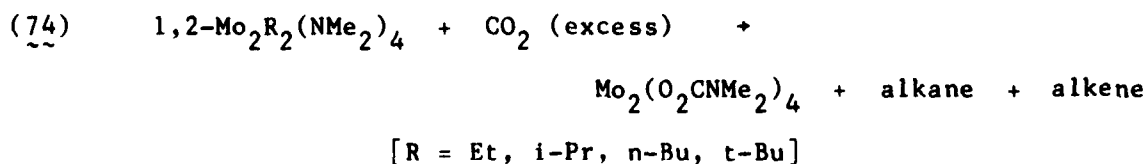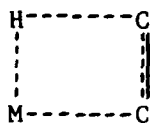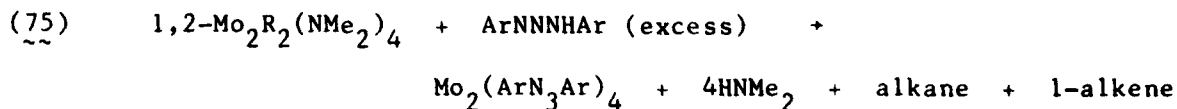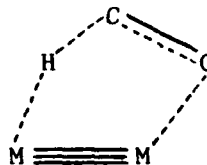
XXXVI   XXXVII

Addition of trialkylphosphines can also induce reduction/elimina-
tion from a dimetal center. For example, addition of PMe_3 to $1,2\text{-}Mo_2Br_2$-
$(CH_2SiMe_3)_4$ gives $Mo_2Br_2(CH_2SiMe_3)_2(PMe_3)_4$. Here a Mo-Mo triple bond is
converted to a quadruple bond, but nothing as yet is known about the
reaction pathway (172). For certain electronic configurations, dinuclear
reduction reactions may reduce M-M bond orders. The quadruply bonded
dimer $Re_2Cl_8^{2-}$ reacts with phosphines to give $Re_2Cl_5(PR_3)_3$ and Re_2Cl_4-
$(PR_3)_4$ compounds containing bonds of order 3.5 and 3.0, respectively
(173).

3.2.3. By Electrochemical Methods

From the oxidative addition and reductive elimination reactions
outlined in sections 3.2.1 and 3.2.2, one might anticipate that it would
be possible to vary metal-metal bond orders electrochemically, by feeding
in or taking out electrons from the various σ, π and δ bonding and
anti-bonding orbitals. Indeed, this proves to be the case, at least for a
number of Re_2^{n+} compounds as is seen in the work of Walton et al.
(173,174,175,176) in Scheme 3.1, which interrelates electrochemical and
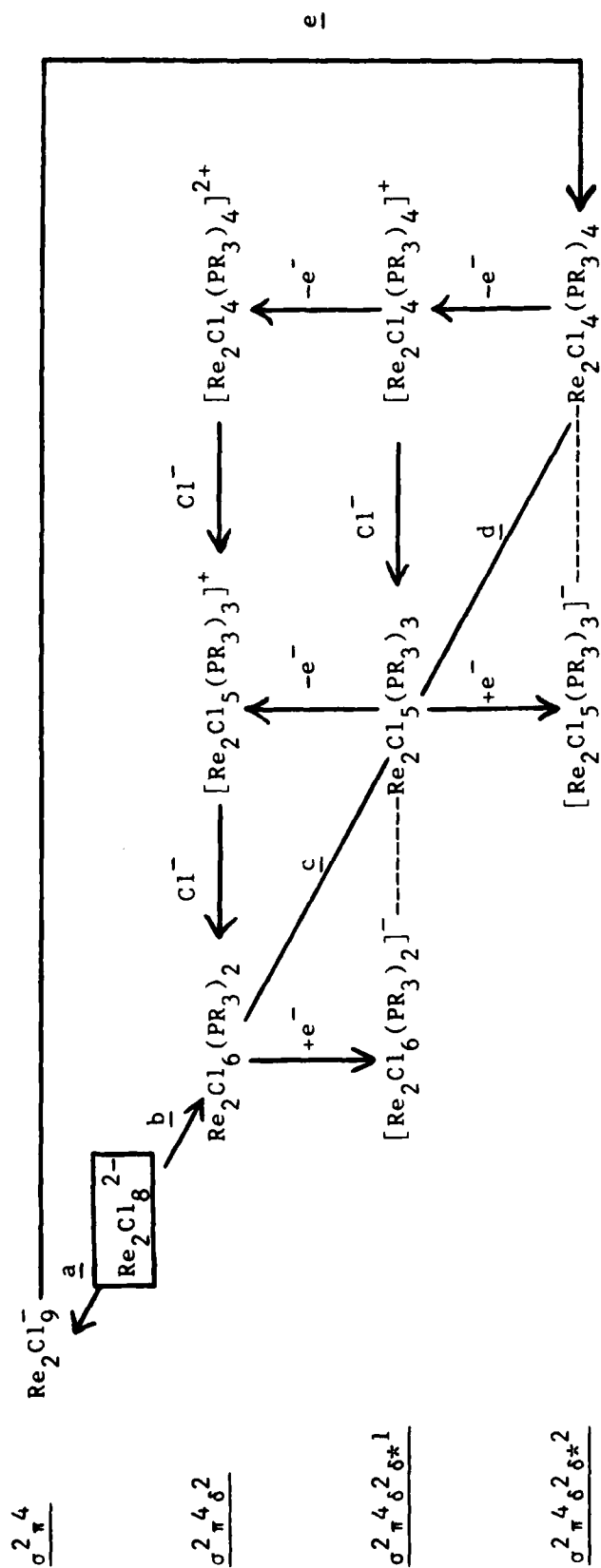
Scheme 3.1 (from 130): Electrochemical oxidations and reductions are represented as $-e^-$ and $+e^-$, respectively, and reaction with chloride ion by Cl^-. Other reactions are as follows: $\underline{a}$, Cl_2 oxidation; $\underline{b}$, reaction with PR_3 at room temperature; $\underline{c}$, reaction with $PRPh_2$ (R = Me or Et) under reflux; $\underline{d}$, reaction with PR_2Ph (R = Me or Et) or PR_3 (R = Me, Et, Pr^n or Bu^n) under reflux; $\underline{e}$, reaction with PEt_3.

chemical oxidations and reductions. Those reactions which remain to be accomplished are represented by dashed, rather than solid, lines.

3.3. Changes in Delocalized Metal-Metal Bonding

For compounds containing three or more metal atoms bonded to each other, so called cluster compounds, it becomes difficult and often quite inappropriate to discuss changes in bonding in terms of localized bonds. Instead, an approach based on delocalized bonding over the whole cluster must be considered. Often a successful entry into bonding schemes for clusters can be made from considerations of symmetry and orbital overlap. Any such qualitative description of the bonding in a cluster must be able to explain the magnetic and structural properties and should be able to rationalize, if not predict, the effects of removing or adding electrons. There are now a number of structurally related cluster compounds which allow these principles to be examined. We have selected tri-, tetra- and hexanuclear cluster compounds arising from the work of Dahl and coworkers, who have pioneered this field.

$Co_3(CO)_9(\mu_3-S)$ and $FeCo_2(CO)_9(\mu_3-S)$

The complex $Co_3(CO)_9(\mu_3-S)$ contains a triangulo group of cobalt atoms, each with three terminal CO ligands, capped by a triply bridging sulfur atom. The molecular structure, determined by a single crystal X-ray diffraction study (177), revealed C_{3v} molecular symmetry. A simple electron count for the molecule reveals that there is one electron too many for an electron precise cluster, i.e. one that satisfies the EAN rule for each metal atom: three Co atoms contribute 27 electrons (3 x 9), nine carbonyl ligands contribute 18 (9 x 2) and the triply bridging

sulfur atom contributes four (it may be viewed as sp^3 hybridized with a lone-pair directed away from the triangulo Co_3 unit) for a total of 49 electrons.

In the symmetry point group C_{3v}, the 15 d orbitals (5 from each Co) can interact to form molecular orbitals: $3a_1 + 2a_2 + 5e$. Using the coordinate system shown in Figure 3.7, three of these molecular orbitals are strongly metal-metal bonding, namely an a_1 and e arising from cobalt d_{z^2} and d_{xz} interactions, respectively. Three molecular orbitals are also strongly anti-bonding, e and a_2 arising from d_{z^2} and d_{xz} interactions, respectively. The remaining 9 molecular orbitals ($2a_1 + a_2 + 3e$) are essentially non-metal-metal bonding. These arise from d_{yz}, d_{xz} and $d_{x^2-y^2}$ interactions. Molecular orbital calculations predict the ordering of molecular orbitals shown in Figure 3.7, which places one electron in the a_2 anti-bonding σ^* M-M orbital. This picture is entirely consistent with the experimental observation that the odd electron sees three equivalent ^{59}Co nuclei, I = 7/2, resulting in a 22 line esr spectrum. Moreover, removal of the odd-electron being in an anti-bonding M-M σ orbital should lead to an increase in M-M bonding. The synthesis of the diamagnetic molecule $FeCo_2(CO)_9(\mu_3-S)$ and its structural characterization bore out these expectations (178,179). There is a net decrease in M-M bond distance of 0.083 Å (averaged). This was the first definitive evidence based on bond length criteria that electrons in excess of the closed shell configuration have strongly anti-bonding character.

$Cp_4M_4(\mu_3-X)_4$ Compounds

The previous example involves a "formal" substitution of Fe for Co into a cluster. By either chemical or electrochemical means, Dahl and

Figure 3.7.   Molecular orbital scheme for the triangulo $Co_3(\mu_3-S)(CO)_9$ molecule.
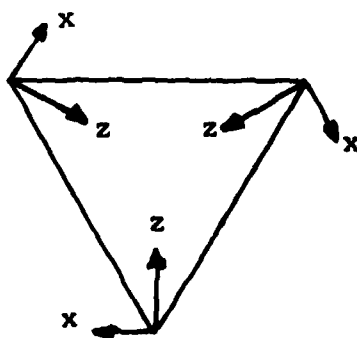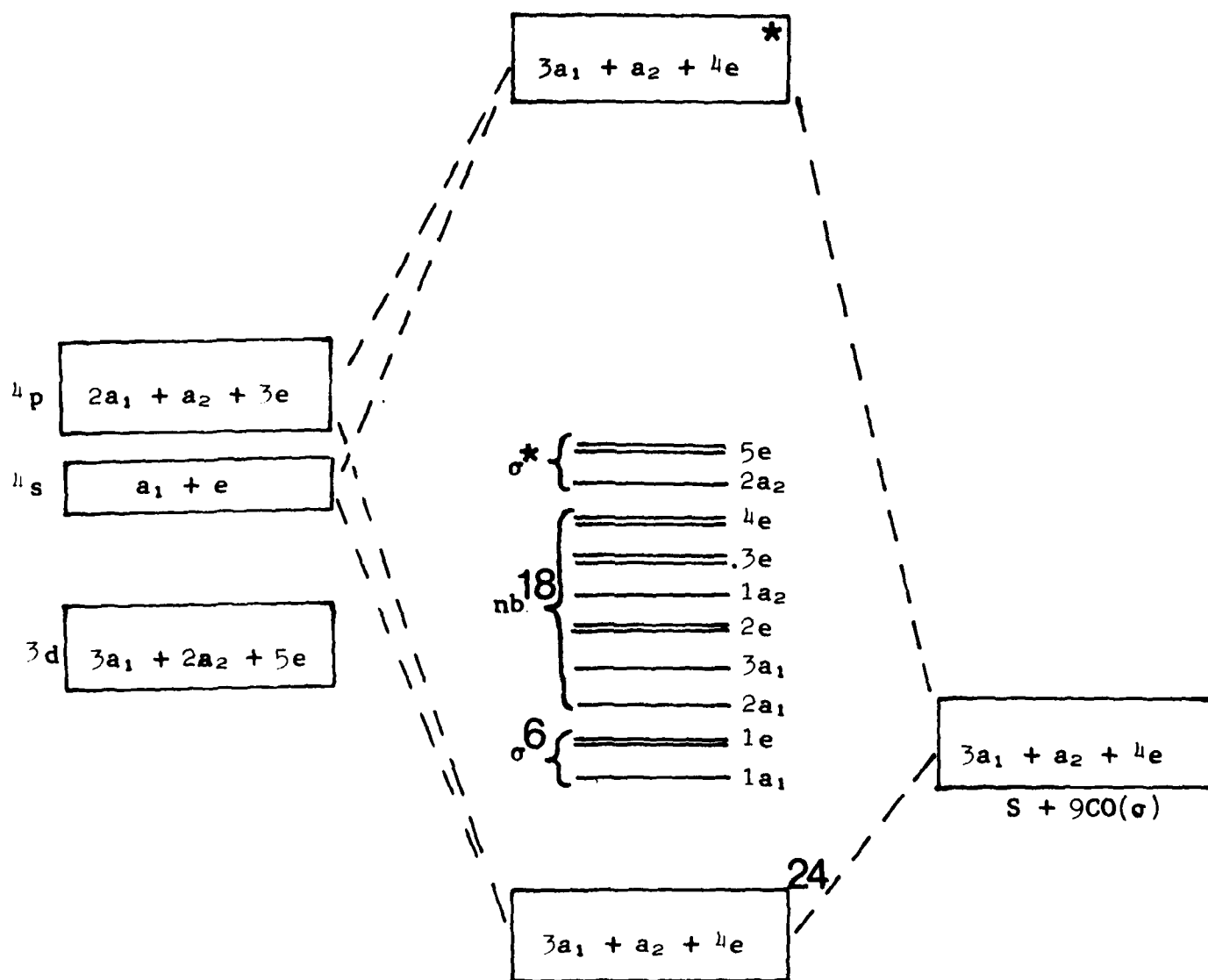
coworkers were able to synthesize and structurally characterize a number of neutral, anionic or cationic cubane complexes of general formula $Cp_4M_4(\mu_3-X)_4$. These include $Cp_4Fe_4(\mu_3-CO)_4^n$, where $n = 0$ and $+1$ (180,181), $Cp_4Fe_4(\mu_3-S)_4^n$, where $n = -1$, 0, $+1$, $+2$, $+3$ (182), $Cp_2Co_4-(\mu_3-S)_4^n$, where $n = 0$ and $+1$ (183) and $Cp_4Co_4(\mu_3-P)_4$ (184).

In the symmetry point group T_d, the 20 d orbitals (5 from each metal atom) give rise to 20 molecular orbitals of symmetry $a_1 + 2e + 2t_1 + 3t_2$. Of these, there are six orbitals of strongly metal-metal bonding character ($a_1 + e + t_2$) and six of strongly anti-bonding M-M character ($t_1 + t_2$). These arise from interactions of the d_{z^2}, d_{xz} and d_{yz} orbitals when the coordinate axes are chosen as shown in Figure 3.8. The d_{xy} and $d_{x^2-y^2}$ orbitals (tangential orbitals) give rise to molecular orbitals ($e_2 + t_1 + t_2$), which are essentially non-bonding with respect to the M_4 unit. (These may be used in bonding to the triply bridging X groups, however, as is seen later.) The metal s and p atomic orbitals give rise to ($a_1 + t_2$) and ($a_1 + e + t_1 + 2t_2$) molecular orbitals, respectively, which are of correct symmetry to interact with the Cp and X ligands. When X - CO, the non-M-M bonding molecular orbitals ($e + t_1 + t_2$) are of correct symmetry to interact with the CO π^* vacant orbitals which transform as E, T_1 and T_2 in the point group T_d. In the case of X = S, the non-bonding M-M orbitals ($e + t_1 + t_2$) will be used in bonding to the sulfur p or sp^3 hybrid orbitals, thus forming a set of bonding and anti-bonding orbitals, as shown in Figure 3.9.

In the case of $Cp_4Fe_4(\mu_3-CO)_4$, there are 24 electrons which occupy Fe_4 cluster molecular orbitals. These fill the bonding and non-bonding orbitals to give an "electron precise" structure with 12 bonding elec-

Figure 3.8. Schematic molecular orbital energy level diagram for the $Cp_4Fe_4(\mu_3-CO)_4$ molecule. The highest energy molecular orbitals which are filled, $[e + t_1 + t_2]$,[16] are involved in backbonding to the CO π^* orbitals and are not significantly involved in M–M bonding.

$a_1 + e + t_1 + 2t_2$ *

$a_1 + t_2$ *

$e + t_1 + t_2$ *

$\pi^*(CO)$

$e + t_1 + t_2$

4p

$a_1 + e + t_1 + 2t_2$

4s

$a_1 + t_2$

$t_1 + t_2$ *

3d

$a_1 + 2e + 2t_1 + 3t_2$

16

$e + t_1 + t_2$

12

$a_1 + e + t_2$

$\pi(Cp)$

$a_1 + e + t_1 + 2t_2$

24

$a_1 + e + t_1 + 2t_2$

$a_1 + t_2$

8

$a_1 + t_2$

$\sigma(CO)$

TETRAMETAL SYMMETRY
ORBITALS

MOLECULAR
ORBITALS

LIGAND SYMMETRY
ORBITALS

x,y

z

x,y

z

x,y

z

z
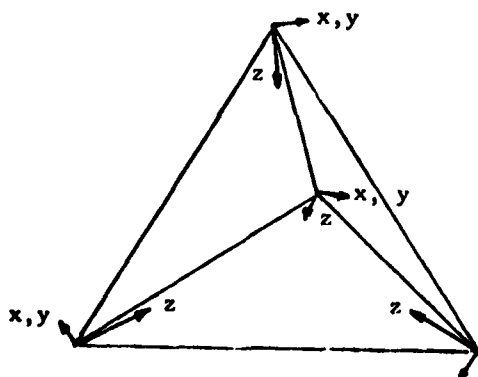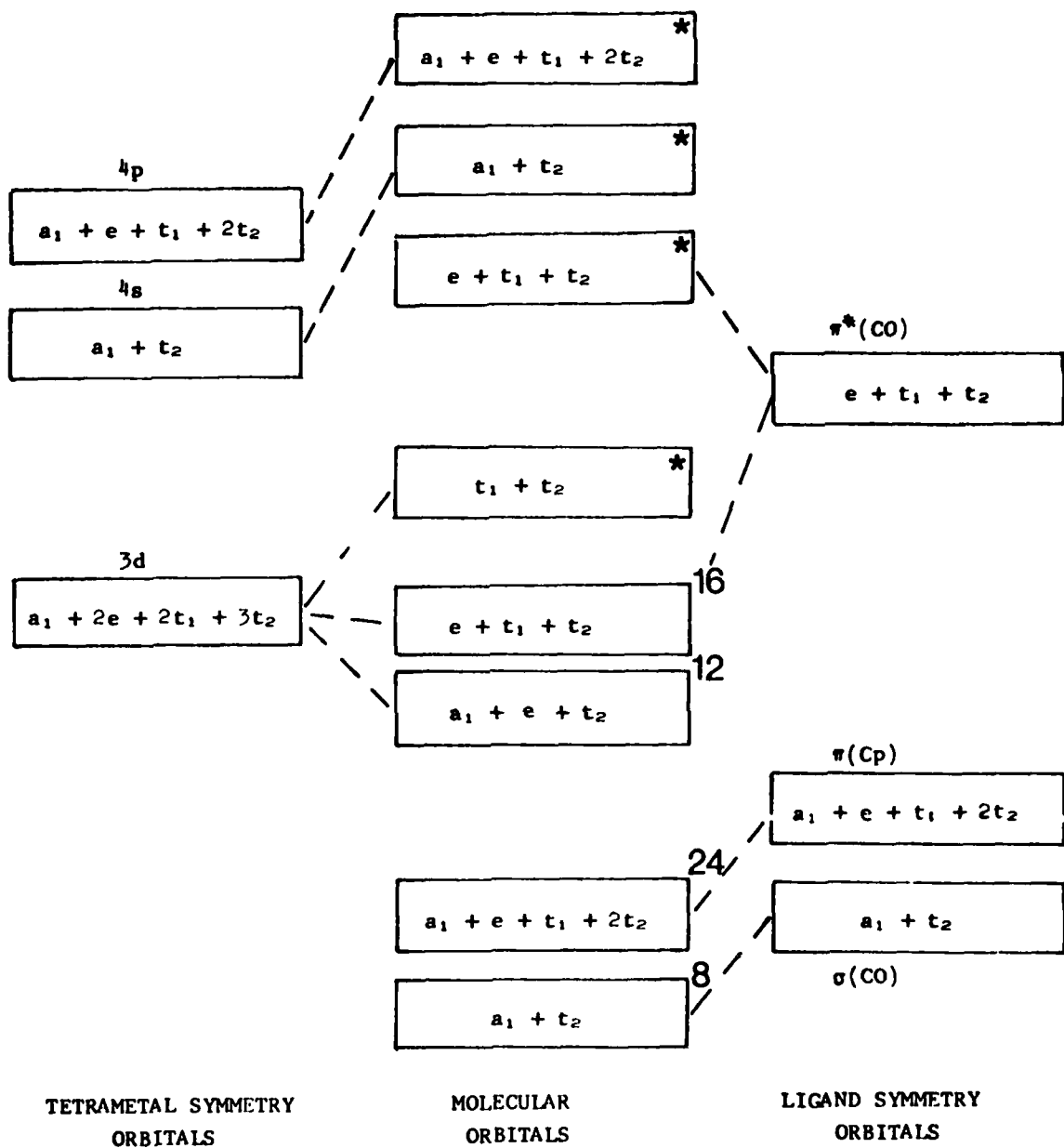
Figure 3.9. Schematic molecular orbital energy level diagram for the $Cp_4Fe_4(\mu_3-S)_4$ molecule. The highest energy occupied molecular orbitals, $[t_1^* + t_2^*]^8$, are antibonding with respect to metal-metal interactions.

TETRAMETAL SYMMETRY   MOLECULAR   LIGAND SYMMETRY
        ORBITALS   ORBITALS   ORBITALS
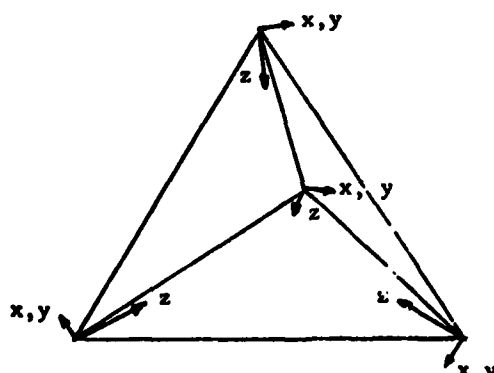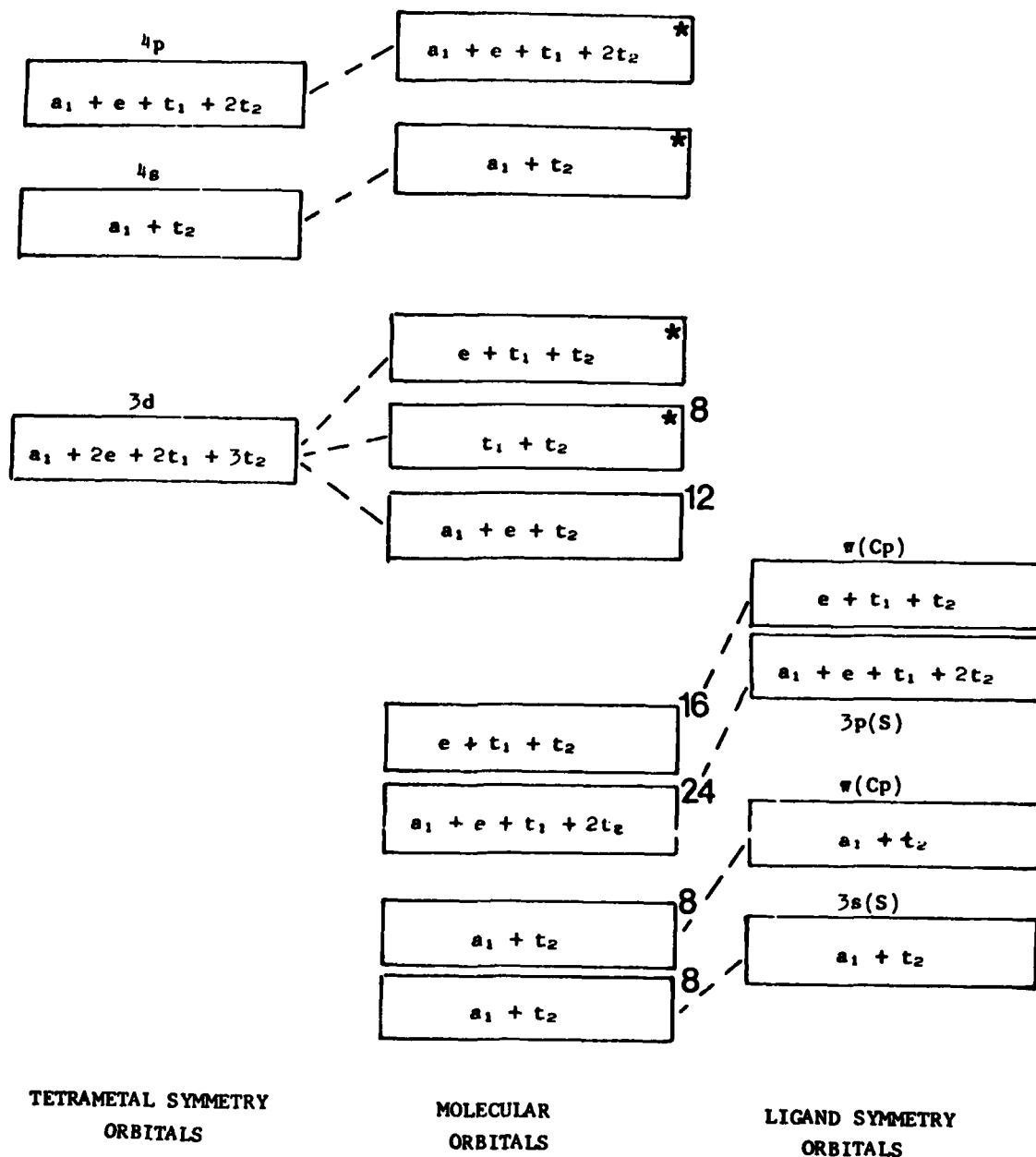
trons in the $(a_1 + e + t_2)$ M-M bonding orbitals, which is equivalent to six electron pair bonds for the tetrahedral Fe_4 unit, Fe-Fe = 2.520 Å. Upon oxidation to the cation $Cp_4Fe_4(\mu_3-CO)_4^+$, very little change occurs in the overall metal-metal bonding as judged by Fe-Fe distances. The most noticeable change occurs in the CO bond order as seen in the C-O distances, which decrease by 0.015 Å (averaged) and $\bar{\nu}(CO)$, which increases by 80 cm^{-1}, with oxidation to the monocation. This is consistent with the view that the electron is removed from an orbital which is non-bonding with respect to the Fe_4 unit, but is involved in back-bonding to the CO π^* orbitals. There is, in fact, a distortion from T_d to D_{2d} symmetry for the Fe_4 unit upon oxidation. This is also consistent with the view that the electron is removed from an orbital of e or t_2 symmetry, which generates a ground state subject to a Jahn-Teller distortion.

A similar story holds for the series $Cp_4Fe_4(\mu_3-S)_4^n$, where n = 0, +1, +2. Since sulfur acts as a four electron donor, the 8 tetrametal non-bonding molecular orbitals of symmetry $e + t_1 + t_2$ are used in M-S bonding and thus, do not lie between the M-M bonding and anti-bonding orbitals. See Figure 3.9. In the neutral molecule, a total of 20 cluster electrons occupy the M-M bonding molecular orbitals $(a_1 + e + t_2)^{12}$ and the anti-bonding molecular orbitals $(t_1 + t_2)^8$. There is a net of four cluster bonding electrons: a Jahn-Teller distortion from T_d symmetry is expected. The molecular structure reveals two short Fe-Fe distances (2.47 Å) and four long Fe-Fe distances (> 3.0 Å) indicative of the formation of two localized M-M σ bonds. Upon oxidation, the long distances get shorter, indicative of an increase in cluster bonding consistent with the removal of electrons from anti-bonding cluster molecular orbitals.

For $Cp_4Co_4(\mu_3-S)_4$, the same schematic molecular orbital energy level diagram is predicted, namely that shown in Figure 3.9. There are, however, 24 electrons available for cluster bonding and these would fill the bonding $(a_1 + e + t_2)^{12}$ and the anti-bonding $(t_1 + t_2)^{12}$ cluster molecular orbitals. A regular tetrahedral complex with no net M-M bonding is expected and is observed; the Co-Co distances are 3.295 Å. Upon oxidation to the mono cation, the molecule distorts from T_d to D_{2d} symmetry, consistent with the removal of an electron from a triply degenerate anti-bonding molecular orbital, either t_1 or t_2. There is also an overall contraction of the Co_4 unit: the average Co-Co distance decreases by 0.12 Å upon oxidation to the mono cation.

Very recently, Dahl et al. (185) reported the preparation of a hexanuclear compound Cp_6Ni_6, formed by reduction of Cp_2Ni with sodium napthalide in THF, and its chemically oxidized (by $AgPF_6$) cation $Cp_6Ni_6^+$, along with their respective structural characterizations. Cp_6Ni_6 is an "electron excessive" cluster (90 electrons) and has four electrons in a t_{2u} anti-bonding M-M molecular orbital in O_h symmetry. The cation $Cp_6Ni_6^+$ has three electrons in the t_{2u} anti-bonding M-M molecular orbital. The structural characterization of these two Ni_6 cluster compounds shows that the latter (the cation) has regular O_h symmetry, whereas the former has a tetragonal distortion. This is entirely consistent with what would be anticipated for t_{2u}^4 and t_{2u}^3 ground states. The former, but not the latter, should be subject to a Jahn-Teller distortion.

4. REACTIONS IN WHICH THE METAL-METAL BONDS ARE ESSENTIALLY UNCHANGED

Compounds containing metal-metal bonds may undergo many of the types of reactions well documented in mononuclear chemistry without any apparent resulting change to the nature of the metal-metal bonds. It should be noted that the intimate mechanism of these reactions may involve intermediates in which the metal-metal bonding is affected, but the net result of the reaction does not reveal this. For the purpose of this article, we shall not catalogue all the various types of reactions of metal-metal bonded compounds, but will concentrate on those in which the reaction path is modified or determined by the presence of the metal-metal framework.

4.1. Substitution Reactions

4.1.1. By Neutral Donor Ligands

As is generally found for mononuclear carbonyl compounds, polynuclear metal carbonyl compounds often show CO ligand substitution chemistry with ligands, such as tertiary phosphines and phosphites, olefins, nitric oxide and CO (self-exchange), by a reaction pathway involving initial M-CO bond cleavage. In some cases, metal-metal bond fission is important (see Section 3.1.1.). With phosphine ligands, stepwise substitution often occurs up to a point, afterwhich extremely harsh conditions are required and these may lead to degradation of the cluster. See equations 74 (186,187), 75 (188) and 76 (189).

(74) $Os_3(CO)_{12} + nPPh_3 \rightarrow Os_3(CO)_{12-n}(PPh_3)_n + nCO$

where n = 1, 2, 3

(75) $H_4Ru_4(CO)_{12}$ + $nPPh_3$ → $H_4Ru_4(CO)_{12-n}(PPh_3)_n$ + nCO

where n = 1, 2, 3, 4

(76) $Ir_4(CO)_{12}$ + $nPPh_3$ → $Ir_4(CO)_{12-n}(PPh_3)_n$ + nCO

where n = 1, 2, 3
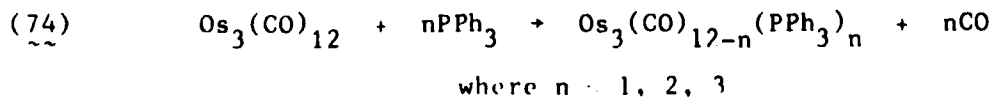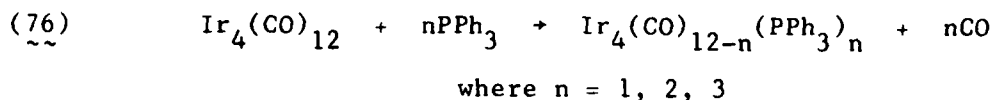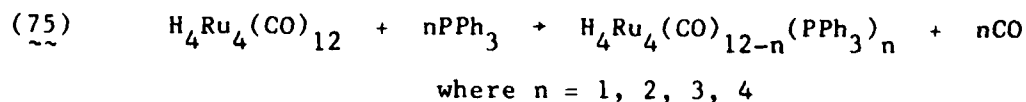
Kinetic studies have shown that in reaction 76, the first replacement of CO to give $Ir_4(CO)_{11}(PPh_3)$ occurs by an associative mechanism, S_N2 and is dependent on phosphine concentration. The second and third CO replacements by PPh_3 are dissociative in nature, S_N1. Both the increase in the dissociative pathway and the increase in rate were explained by the formation of bridging CO ligands.

Substitutions of CO, by less sterically demanding isonitrile ligands, tend to proceed further than related phosphine substitution reactions, as is seen in reaction 77 (190).

(77) $Co_4(CO)_{12}$ + $5Bu^tNC$ → $Co_4(CO)_7(Bu^tNC)_5$ + $5CO$
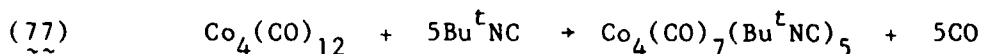
Substitution reactions of polynuclear metal carbonyls can be complicated by the large number of isomers which may be formed. For a non-bridged molecule of formula $Os_3(CO)_{10}L_2$, some 10 isomers are possible, as is shown in Figure 4.1. Structural studies have shown that phosphine substituents prefer to occupy equatorial sites and this has been ascribed as a steric effect (191). However, in the case of the isonitrile substituted products $Os_3(CO)_{12-n}(NCR)_n$, where R = Me and $p-C_6H_4OMe$ and n = 1, 2 or R = Bu^n and Bu^t and n = 1, 2, 3, 4, ^{13}C nmr studies have shown that a preference for axial substitution is more favorable when steric crowding is absent (192).
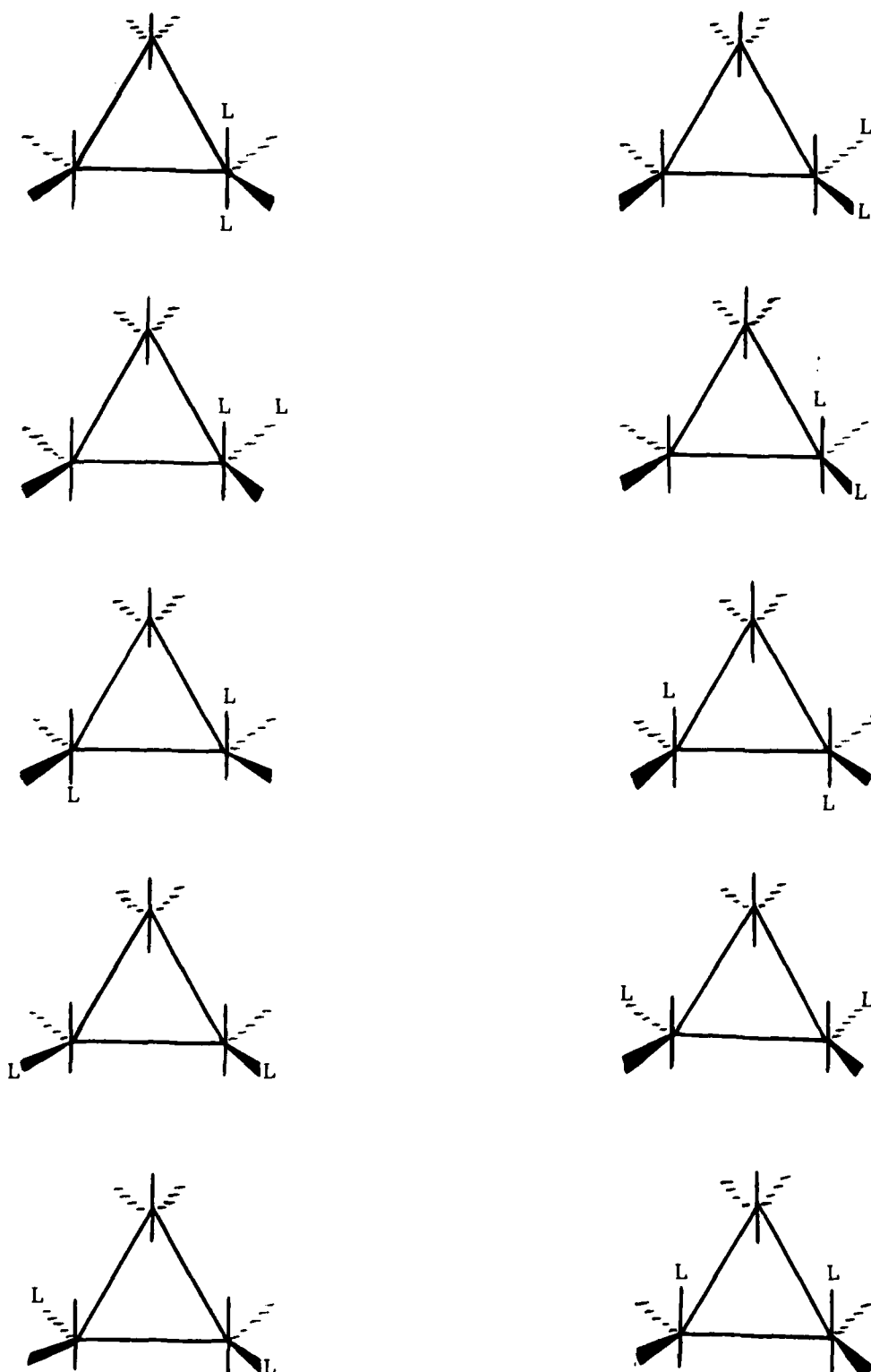
Figure 4.1. The ten possible isomers which arise for $Os_3(CO)_{10}L_2$ molecules in the absence of carbonyl bridging.

The conditions which are required to allow CO substitution by olefins are often sufficient to allow further activation and breakdown of the hydrocarbon. Thus, although $Os_3(CO)_{12}$ reacts with ethylene at elevated temperatures, the product is not a simple substitution product, but $H_2Os_3(CO)_9(C=CH_2)$, in which ethylene has been broken down to give hydrido and vinylidene ligands (193). By using the reagent Me_3NO, which oxidizes CO to CO_2 and leaves a weakly coordinating, and easily displaced, Me_3N ligand, the simple ethylene substitution product $Os_3(CO)_{11}$-(C_2H_4) has been made at lower temperatures and, furthermore, this has been shown to be an intermediate in the formation of $H_2Os_3(CO)_9(C=CH_2)$ (194).

In the case of alkynes, substitution of CO does not lead to simple adducts in which the alkyne acts as a monodentate 2e donor. In dinuclear chemistry, the reactions proceed to give substitution of two CO ligands as in the formation of $Co_2(CO)_6(\mu-C_2Ph_2)$ in the reaction between $Co_2(CO)_8$ and $PhC \equiv CPh$ (195).

For trinuclear clusters, two modes of alkyne coordination have been observed. In $Os_3(CO)_{10}(PhCCPh)$, the acetylene unit may be described as a dimetal substituted alkene, containing two M-C σ bonds and an η^2-olefin bond to the other metal, XXXVIII (196).

XXXVIII
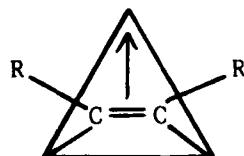
In $Fe_3(CO)_9(PhCCPh)$, the acetylene is arranged over one edge of the triangle of metal atoms, as in XXXIX (197).

XXXIX
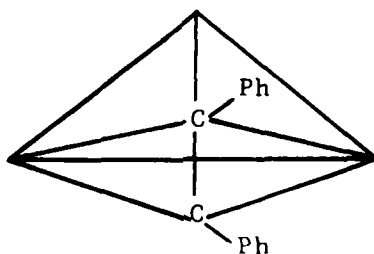
These two types of M_3-alkyne clusters have been described as <u>nido</u> (XXXVIII) and <u>closo</u> (XXXIX), respectively.

The tetranuclear cluster $Co_4(CO)_{12}$ reacts with acetylenes to give $Co_4(CO)_{10}(C_2R_2)$, in which the alkyne acts as a four electron donor to the Co_4 unit, which opens up to a Co_4 butterfly, as shown in XL (198).

XL
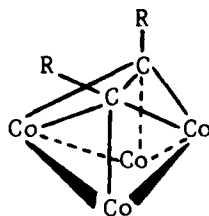
Substitution of an anionic ligand by a neutral or different anionic ligand is also well known for dinuclear and polynuclear metal compounds. For example, the $Mo_2Cl_8^{4-}$ anion reacts with tertiary phosphines to give neutral compourds of formula $Mo_2Cl_4L_4$ with retention of the $Mo{\equiv}Mo$ bond (74,199). Structural studies reveal the presence of eclipsed trans $MoCl_2$-L_2 units joined by the $Mo{\equiv}Mo$ bond in the manner shown in XLI.

XLI
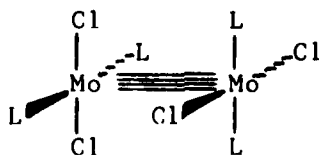
Presumably, this geometry results from the minimization of steric repulsive interactions. The use of bulky phosphine ligands in weakly coordinating solvents, such as methanol, has led to the isolation of solvento complexes, e.g. $Mo_2Cl_4(PPh_3)_2(MeOH)_2$, in which one of the ligands L in XLI is replaced by a solvent molecule at each molybdenum atom (81).

Both molybdenum and tungsten compounds $M_2Cl_4(PBu^n_3)_4$ undergo substitution with bidentate phosphines to give compounds of formula $M_2Cl_4-(L-L)_2$, which fall into two structural types, namely those with unbridged $M\equiv M$ bonds, in which the bidentate phosphine acts as a chelating ligand to one metal atom, and those with bridged $Mo\equiv Mo$ bonds. The latter are generally favored when the bridge forms a five-membered ring as is seen in Table 4.1.

The related rhenium dimer $Re_2Cl_8^{2-}$ ($M\equiv M$) reacts with monodentate phosphines to give products of reduction $Re_2Cl_4L_4$ and $Re_2Cl_5L_3$ (see Section 3.2.2). With bidentate phosphines, products of substitution, $Re_2Cl_6(dppe)$ and $Re_2Cl_4(dppe)_2$, have been isolated from reactions involving $Re_2Cl_8^{2-}$ and $Re_2Cl_4(PEt_3)_4$ with dppe, respectively (121). These compounds have been shown by X-ray structural characterization to have bridging dppe ligands (203).

4.1.2. By Protolysis

The reaction of protic groups YH with M-X bonds can lead to substitution: M-X + YH $\rightleftharpoons$ M-Y + XH. The position of equilibrium and the utility of this type of reaction depend on the strengths of the M-X and M-Y bonds, the acidities of XH and YH and on the solubilities and/or

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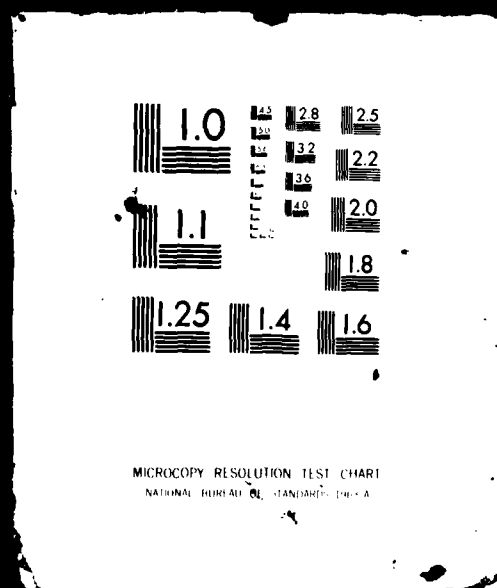
Table 4.1. Structural Types of $M_2Cl_4(L-L)_2$ Compounds.

compound[a]	unbridged	bridged	ref.
$Mo_2Cl_4(dppm)_2$		*	200
$Mo_2(NCS)_4(dppm)_2$		*	200
$W_2Cl_4(dmpe)_2$	*		70
$W_2Cl_4(dppe)_2$ green	*		70
$W_2Cl_4(dppe)_2$ brown		*	70
$Mo_2Br_4(arphos)_2$		*	201
$Mo_2Cl_4(dppe)_2$	*		202
$Mo_2Cl_4(dppe)_2$		*	202

[a] dppm = $Ph_2CH_2PPh_2$; dmpe = $Me_2PCH_2CH_2PMe_2$; dppe = $Ph_2PCH_2CH_2PPh_2$; arphos = $Ph_2AsCH_2CH_2PPh_2$.

volatilities of the M-X, M-Y, XH and YH species. A large number of examples of this type of reaction are known and are well illustrated by reactions 78 (83), 79 (204), 80 (205), 81 (206) and 82 (207), in which metal-to-metal triple bonds are preserved.

(78) $Mo_2(NMe_2)_6 + 6ROH \rightarrow Mo_2(OR)_6 + 6HNMe_2$

$[R = Bu^t, PhMe_2C, Me_2CH, CH_2CMe_3]$

(79) $Mo_2(CH_2SiMe_3)_6 + 2HBr \rightarrow Mo_2Br_2(CH_2SiMe_3)_4 + 2Me_4Si$

(80) $1,2-Mo_2Br_2(CH_2SiMe_3)_4 + 4HNMe_2 \rightarrow$

$1,2-Mo_2(NMe_2)_2(CH_2SiMe_3)_4 + 2Me_2NH_2Br$

(81) $W_2(NMe_2)_6 + 2PhNNNHPh \rightarrow W_2(NMe_2)_4(PhN_3Ph)_2 + 2HNMe_2$

(82) $W_2(O_2CNMe_2)_6 + 6CO_2 \rightarrow W_2(O_2CNMe_2)_6$
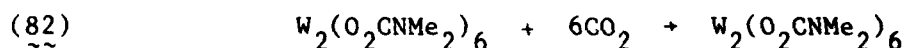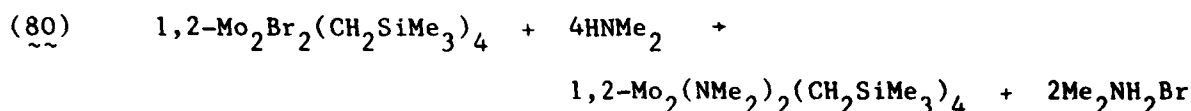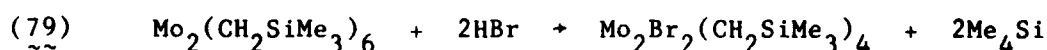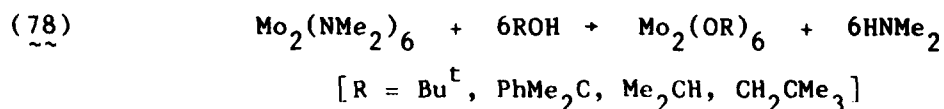
Although 82 involves the overall insertion of CO_2 into $W-NMe_2$ bonds, it occurs by an amine catalyzed sequence in which dimethylcarbamic acid displaces dimethylamine (208): $Me_2NH + CO_2 \rightleftharpoons Me_2NCOOH$; $M-NMe_2$ + $HOOCNMe_2 \rightarrow MO_2CNMe_2 + Me_2NH$. The triazenido and carbamato ligands act as bidentate ligands to the dimetal center without disrupting the $M \equiv M$ bond, since the metal atoms do not achieve an 18 valence shell of electrons. The bidentate groups may chelate to one metal or may bridge both depending upon steric considerations. In $W_2(O_2CNMe_2)_6$, both bridging and terminally bonded O_2CNMe_2 ligands are seen.

4.1.3. By Metathetic Exchange Reactions

The exchange of anionic ligands between two metal atoms provides a particularly successful approach to substitution when one product is

insoluble. This is the situation when organolithium reagents react with transition metal halo complexes, as is seen in reactions $\underset{\sim\sim}{83}$ (209), $\underset{\sim\sim}{84}$ (210), $\underset{\sim\sim}{85}$ (211) and $\underset{\sim\sim}{86}$ (212).

$(\underset{\sim\sim}{83})$ $\qquad M_2Cl_2(NMe_2)_4 + 2LiR \rightarrow M_2R_2(NMe_2)_4 + 2LiCl$

$\qquad$ [M = Mo, W; R = Me, Et, n-Bu, s-Bu, t-Bu, i-Pr, CH_2SiMe_3]

$(\underset{\sim\sim}{84})$ $\qquad Re_3Cl_9 + 6LiCH_2SiMe_3 \rightarrow Re_3Cl_3(CH_2SiMe_3)_6 + 6LiCl$

$(\underset{\sim\sim}{85})$ $\qquad Mo_2(OAc)_4 + 8LiMe \rightarrow Li_4[Mo_2Me_8] + LiCl$

$(\underset{\sim\sim}{86})$ $\qquad Mo_2(OAc)_4 + 4$ $\rightarrow Mo_2(hmmp)_4 + 4LiOAc$
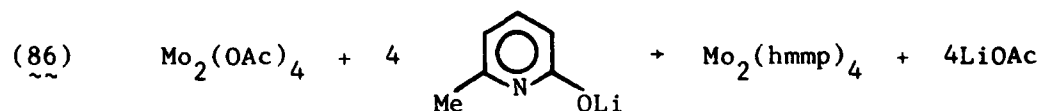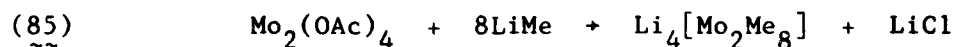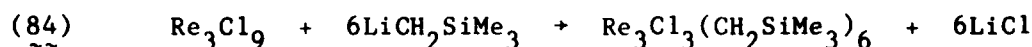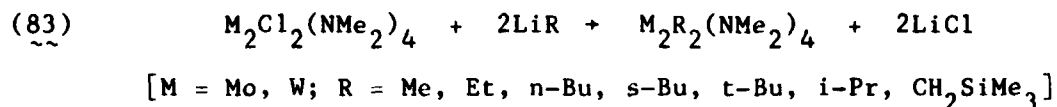
Relatively little is known about the mechanisms of these types of exchange reactions, but some findings indicate that this should prove an interesting area for future research. For example, it was found that anti-1,2-$W_2Cl_2(NEt_2)_4$ and MeLi (2 equiv) react to give initially anti-1,2-$W_2Me_2(NEt_2)_4$, which then isomerizes to the gauche rotamer (213). This implies that exchange occurs with retention of configuration at tungsten and is reconcilable with a four center transition state, XLII.

XLII $\qquad$
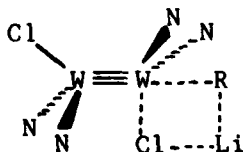
However, the seemingly related reaction between 1,2-$Mo_2Br_2(CH_2Si-Me_3)_4$ and $LiNMe_2$ (2 equiv) gives 1,1-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$, in which an alkyl group transfer has occurred. The 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ isomer

is formed in 80. Once formed, these isomers have not been observed to isomerize!

4.2. Insertion Reactions

As with mononuclear compounds, the insertion of unsaturated molecules into M-X bonds can occur, but in dinuclear or polynuclear chemistry, the products may be stabilized by coordination of the unsaturated moiety to more than one metal atom. For example, $Os_3(CO)_{10}(\mu-H)_2$ reacts with ethyne to give the hydrido vinyl compound XLIII (196).

XLIII
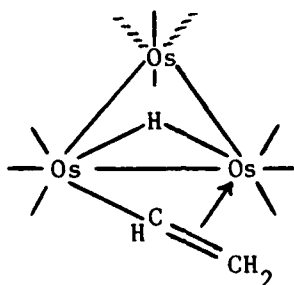
Similarly, $Os_3(CO)_{10}(\mu-H)_2$ reacts with ketenes to give XLIV (214).

XLIV
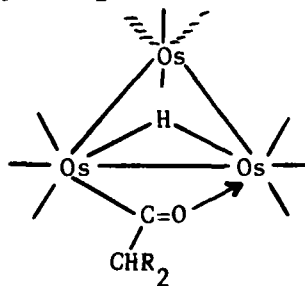
Although $Re_2(CO)_8H_2$ reacts with rupture of the Re-Re bond, the ligand bridged compound $Re_2(\mu-H)_2(CO)_6(dppm)$ reacts with acetonitrile to give a mixture of isomers XLV and XLVI, in which the partially hydrogenated nitrile is bound to both metal atoms (160).

XLV   XLVI
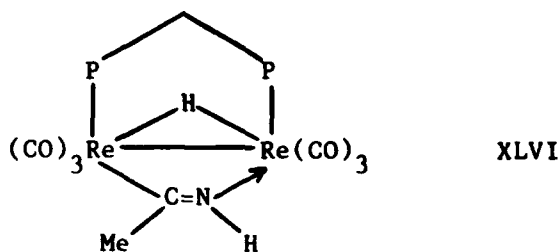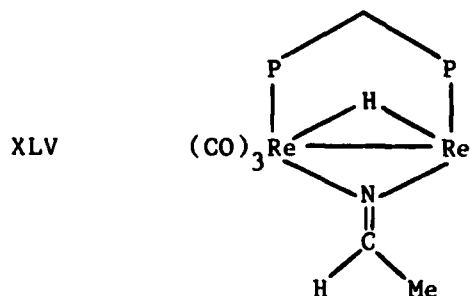
Insertion reactions involving other than metal hydride ligands are less well documented, but are known. For example, carbon dioxide reacts reversibly with the dinuclear alkoxides of molybdenum and tungsten according to 87. In contrast to the insertion reactions of CO_2 and $M_2(NMe_2)_6$ compounds (reaction 82), which are catalyzed by the presence of free amine, reaction 87 proceeds via a direct insertion mechanism (215).

(87) $M_2(OR)_6 + 2CO_2 \rightleftharpoons MO_2(OR)_4(O_2COR)_2$
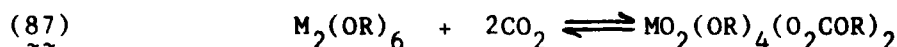
4.3. Addition Reactions

An electron precise organometallic cluster may undergo addition reactions without any change in metal-metal bonding only when there is a concomitant or initial loss of another ligand. Normally, additions involve X-H bonds and by far the most important are those involving C-H bonds. The close proximity of other metal centers in cluster compounds can assist in achieving the correct configuration for X-H or X-X bond activation and, furthermore, the multinuclear framework may stabilize organic fragments by multidirectional bonding. This type of reactivity is well exemplified in triosmium chemistry where the triangle of metal atoms is the smallest of clusters.

Treatment of $Os_3(CO)_{12}$ with aniline, $PhNH_2$, leads to loss of two CO ligands with the formation of $HOs_3(CO)_{10}(\mu\text{-NHPh})$, XLVII.

XLVII
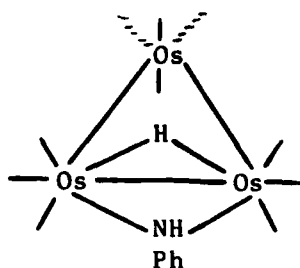
Upon heating XLVII above 150°C, another carbonyl ligand is lost and competition occurs between addition of another N-H bond, giving XLVIII, and addition of the ortho-C-H bond of the phenyl group, giving XLIX (216).

XLVIII

$H_2Os_3(CO)_9(NPh)$

XLIX

$H_2Os_3(CO)_9(HNC_6H_4)$
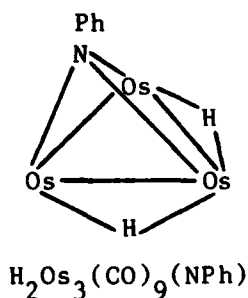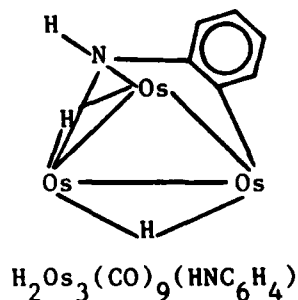
The compound $HOs_3(CO)_9(CH_3)$, L, has been shown to possess a three-electron donating bridging CH_3 group in which a three-center, two-electron M-H-C interaction takes place (217). The compound isomerizes to $H_2Os_3(CO)_{10}(CH_2)$, LI, a process involving addition of the C-H bond.

L
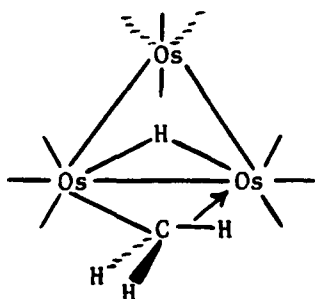
LI
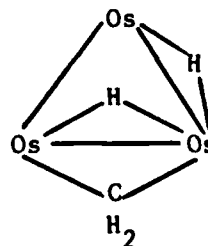
At higher temperatures, another carbonyl ligand is lost, to give $H_3Os_3(CO)_9(\mu_3\text{-}CH)$, LII (217).

LII
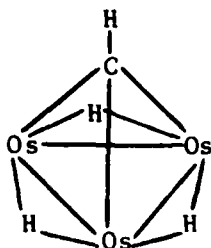
Besides X-H bonds, P-C and As-C bonds are well known to undergo addition. For example, the substitution reaction between PPh_3 and Os_3- $(CO)_{12}$ leads initially to $Os_3(CO)_{11}(PPh_3)$, which upon thermolysis, yields (186) $HOs(CO)_8(\mu_2-PPh_2)(\mu_3-C_6H_4)$, LIII. The μ_3-benzyne ligand may be viewed as the product of an ortho-C-H metallation reaction followed by a P-C addition, which also generates the μ_2-phosphido ligand.

LIII
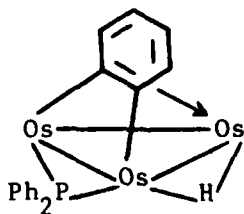
5. FLUXIONAL BEHAVIOR OF METAL-METAL BONDED COMPOUNDS

5.1. General Considerations

Fluxional processes can be broken down into the following categories:

(1) Intramolecular motion of the ligands about the metal atom(s).

(2) Intermolecular exchange of ligands.

(3) Motion about metal-ligand bonds.

(4) Intramolecular rearrangements of the metal-metal bonds.

(5) Intermolecular exchange of metal atoms.

(6) Motion about metal-metal bonds.

Categories 1, 2 and 3 are common to mono and polynuclear compounds, while 4, 5 and 6 are unique to metal-metal bonded compounds. For the purpose of this review, the latter group are considered of major importance, although it must be recognized that the presence of more than one metal center can greatly modify the mobility of ligands. The dynamic behavior of ligands at polynuclear metal centers has recently been reviewed (218). Stereochemical lability involving the metal-metal bonds is less well documented. In some systems, this process may be degenerate with ligand migrations. One of the most studied fluxional processes of polynuclear compounds is carbonyl scrambling. A recent treatment of this phenomenon in binary metal carbonyls has considered a metal atom cluster within a polyhedron of carbonyl ligands. Mutual orientations of the two, or rearrangements of the ligand polyhedra along reaction coordinates, are then used to explain the observed exchange processes (219,220,221). However, skeletal rearrangements of the metal atom cluster are not considered.

5.2. Intramolecular Rearrangements of Metal-Metal Bonds

The only unequivocal observation of intramolecular rearrangements of metal-metal bonds is by nmr studies and only recently have such studies been applied to this problem. The two metal nuclei most studied in polynuclear metal-metal rearrangements are ^{103}Rh ($I = \frac{1}{2}$, 100% natural abundance) and ^{195}Pt ($I = \frac{1}{2}$, 34% natural abundance).

The compound $[Rh_9P(CO)_{21}]^{2-}$ contains a mono capped cube-antiprism of rhodium atoms with an intersticial phosphorus atom. See Figure 5.1. There are three types of rhodium atoms in the solid state, Rh(1), Rh(2) and Rh(3) in Figure 5.1. The ^{31}P nmr spectrum of the compound at $+35°C$ shows a 10-line pattern, indicative of coupling to nine equivalent ^{103}Rh nuclei, whereas at $-80°C$, the spectrum is considerably more complex. This was interpreted in terms of metal atom fluxionality: at $+35°C$, the phosphorus atom sees nine equivalent rhodium atoms on the nmr time scale (222). The unequivocal proof for this process came from the ^{103}Rh nmr spectra. At $-90°C$, there were three resonances in the integral ratio 4:4:1, each being coupled to ^{31}P, $I = \frac{1}{2}$. At $+27°C$, only one ^{103}Rh resonance was observed at an averaged chemical shift value of the low temperature resonances. Coupling to ^{31}P was not lost during the coalescence, thereby establishing an intramolecular process (223).

^{195}Pt nmr studies have been carried out on some of the $[Pt_3(CO)_9]_n^{2-}$ clusters. For $n = 3$, the ^{195}Pt nmr spectra show that rapid rotation is occurring between the stacked triangulo-Pt_3 units, resulting in two ^{195}Pt signals of relative intensity 2:1, with the statistically expected coupling to 3 and 6 ^{195}Pt atoms, respectively (224). No exchange between inner and outer Pt_3 triangles is observed or between inner and outer CO ligands.

5.3. Intermolecular Exchange of Metal Atoms

The platinum clusters $[Pt_9(CO)_{18}]^{2-}$ and $[Pt_{12}(CO)_{24}]^{2-}$ have been shown to interact in solution, leading to a broad ^{195}Pt nmr signal at $25°C$. This has been ascribed to an intermolecular exchange process, 88 (224), but the system has not been well characterized.

Figure 5.1.   The Rh_9P skeleton of the $[Rh_9P(CO)_{21}]^{2-}$ anion showing the three types of rhodium atoms.

P

Rh(1)

Rh(2)

Rh(3)

(88) $[Pt^*_{12}(CO)_{24}]^{2-}$ + $[Pt_9(CO)_{18}]^{2-}$ $\rightleftharpoons$

$[Pt_9Pt^*_3(CO)_{24}]^{2-}$ + $[Pt^*_9(CO)_{18}]^{2-}$
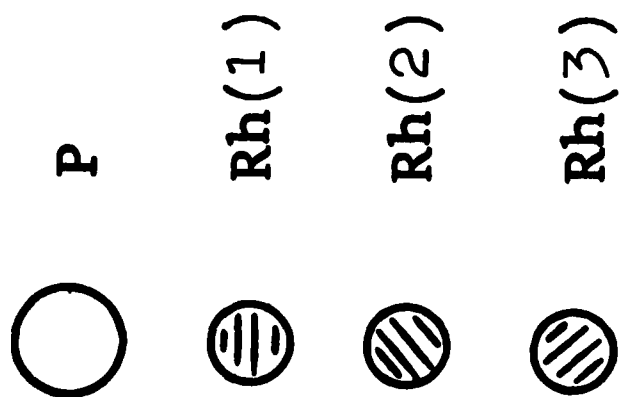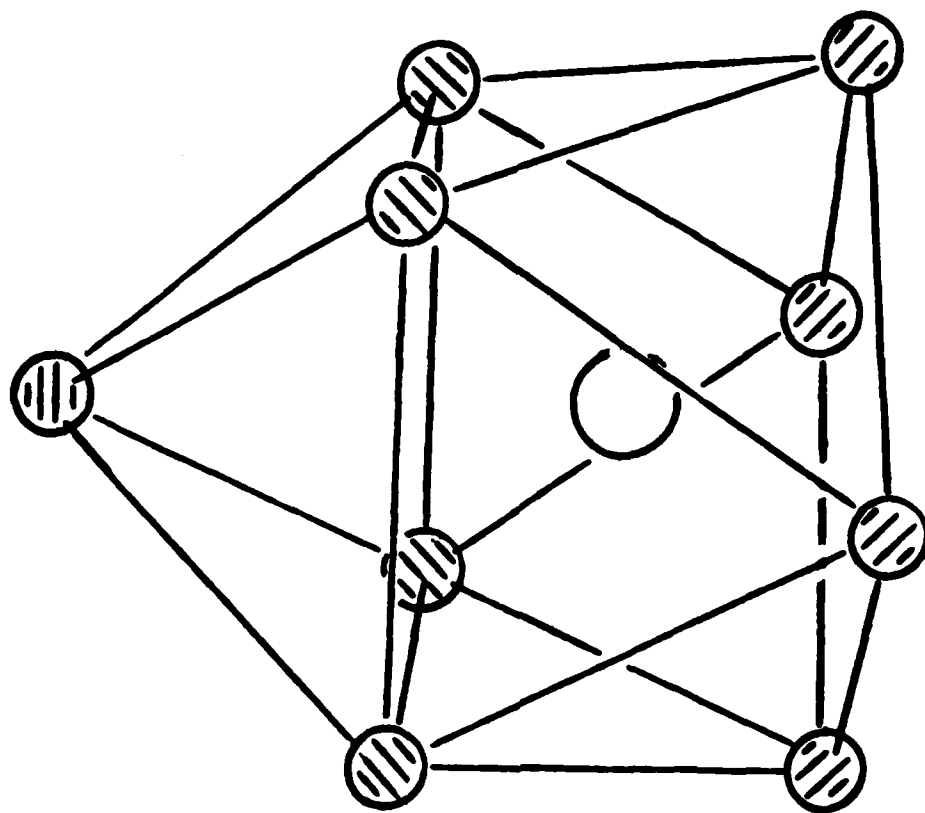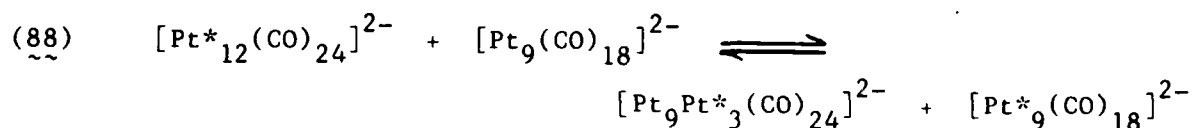
5.4. Rotations about Metal–Metal Bonds in Dinuclear Complexes

5.4.1. Single Bonds

For dinuclear compounds containing unbridged metal–metal σ bonds, there is no electronic barrier to rotation. However, the presence of bulky substituents on the metal atoms can lead to quite sizeable steric barriers to rotation about these bonds. For example, the compounds $Cp_2M_2(CO)_6$ (M = Cr, Mo, W) exist in anti and gauche rotamers and exchange between these two forms have barriers of 51 (Cr), 63 (Mo) and 68 kJ mol^{-1} (W). The increase from chromium to tungsten is as expected from the bond lengths (Cr–Cr > Mo–Mo > W–W), although the large disparity between chromium and the other two compounds may be due to some contribution from metal–metal bond breaking for the chromium compound (151).

For bridged metal–metal single bonds, as in $Cp_2Fe_2(CO)_4$, two forms have been identified in the solid state: cis (225) and trans (226). Exchange of bridge and terminal carbonyl ligands and cis and trans isomerizations have been observed with various activation energies. These observations have been rationalized in terms of a two-step process: an initial facile bridge, opening to form a non-bridged molecule, followed by rotation about the Fe–Fe bond (227).

5.4.2. Double Bonds

At the present time, no unequivocal observation of rotation about a metal–metal double bond has been made. One would expect that the presence

of a π-component ($\sigma^2 \pi^2$) would impose a sizeable electronic barrier when the π bond is not degenerate, as is the case for olefins. However, although a number of M–M double bonded compounds are known, they all have bridging groups (this destroys the degeneracy of the π_x, π_y orbitals). Exchange of bridge and terminal ligands has been observed, e.g. for $Mo_2(OPr^i)_8$ (33), but this need not involve disruption of the π bond.

5.4.3. Triple Bonds

Because of the cylindrical nature of a $\sigma^2 \pi^4$ triple bond, there should be no electronic barrier to rotation. Only recently, however, has a direct observation of rotation about an element–element triple bond been made. [For $C \equiv C$ and $C \equiv N$ bonds, the presence of linearly aligned σ bonded substituents makes it impossible to factorize rotations about *terminal σ bonds from the central triple bond.*] Compounds of the type $1,2-M_2X_4Y_2$ (M = Mo, W) exist in anti and gauche forms. The mixed alkyl dialkylamido compounds $1,2-M_2R_2(NMe_2)_4$ show barriers to rotation of ca. 20–25 Kcal mol^{-1}, while the less sterically encumbered molecules 1,1- and $1,2-Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ have rotational barriers of 15 Kcal mol^{-1}, which allow observation of $M \equiv M$ rotation on the nmr time scale (204,205). The NMe_2 ligands act as cogs and impose steric barriers to rotation. For the compounds $1,2-Mo_2X_2Y_2$, where X = Me, OBu^t and Y = CH_2SiMe_3, and X = Me and Y = OBu^t, and $Mo_2Br(CH_2SiMe_3)_5$, rotation about the $Mo \equiv Mo$ bond is sufficiently facile that it has not been frozen out on the nmr time scale, even at low temperatures.

5.4.4. Quadruple Bonds

The addition of a δ component to the cylindrical triple bond $(\sigma^2\pi^4)$ should lead to an electronic barrier to rotation in compounds of the type $Mo_2X_4L_4$ (X = uninegative ligand, L = neutral donor), where the degeneracy of the $d_{x^2-y^2}$, d_{xy} orbitals is removed. The observed eclipsed geometries are consistent with this line of reasoning, but at this time, no value for the barrier to rotation about a $M\equiv M$ bond has been experimentally determined.

6. CATALYSIS INVOLVING METAL–METAL BONDED COMPOUNDS

6.1. General Considerations

The number of homogeneous catalytic systems in which the active catalyst has been shown to be a di- or polynuclear metal compound is very small. Although the initial form of the catalysts may be polynuclear, there is, in nearly all cases, no evidence to suggest that the polynuclear integrety is maintained during the reactions (228). Indeed, in a large number of cases, the active catalyst has been shown to be mononuclear (229). In some cases, however, it is found that the catalytic reaction cannot be carried out by known mononuclear compounds, but requires that the catalyst precursor be polynuclear. This is the case for $Ni_4(CNBu^t)_7$, which promotes a variety of hydrogenation reactions not observed when $Ni(CNBu^t)_4$ is used (230).

Another problem arises for reactions run at very high temperatures: thermal decomposition of the cluster may lead to the formation of finely divided metal. The catalytic reaction may then be a heterogeneous one,

although upon cooling and work up, the cluster compound may be reformed. This is believed to be the situation in the production of alkanes from CO/H_2 in the presence of $Ru_3(CO)_{12}$ (229).

One important process where the active catalyst is believed to be a cluster is the Union Carbide patented syntheses of ethylene glycol from CO/H_2 at 200-300°C, 1,000 to 3,000 Atmos. The active catalyst is believed to be either a Rh_{12} or Rh_{13} containing species (231).

By far the best documented examples of catalysis involving non—mononuclear species are seen in the reactions of alkynes at dimetal centers. Even here, however, mononuclear species, such as $(PhCN)_2PdCl_2$ and $CpCo(CO)_2$, are capable of carrying out equivalent polymerization, cyclotrimerization and hydrogenation reactions (232).

6.2. Reactions of Alkynes at Dimetal Centers

The compound $Cp_2Mo_2(CO)_4$ contains a $Mo\equiv Mo$ bond and will react with alkynes to form adducts $Cp_2Mo_2(CO)_4(RCCR')(Mo-Mo)$ (153). In the presence of hydrogen and acetylene above 100°C, this compound will catalyze the production of the cis-olefin. A first order rate law is observed and the first step is believed to involve dissociation of CO to give $Cp_2Mo_2(CO)_3(RCCR)$. Labelling studies conclusively showed that no fragmentation of the dinuclear complex was involved during the catalytic cycle (166).

The direct interaction of alkynes with $Cp_2Mo_2(CO)_4(RCCR)$ compounds in the absence of hydrogen has been shown to lead to $M_2C_4R_4$, $Mo_2C_4R_6$ and $M_2C_8R_8$ containing species (233,234). The oligomerization of the alkyne units around the dimetal center suggests a plausible pathway for alkyne polymerization at a dinuclear center. Similar chemistry had been noted for reactions involving $Co_2(CO)_8$ and alkynes several years ago (235).

The compounds $Mo_2(OR)_6$, where $R = Pr^i$ and Ne (CH_2CMe_3), which contain Mo-Mo triple bonds, but in other way are rather different from the aforementioned organometallic dinuclear compounds, have recently been found to polymerize acetylenes rapidly at room temperature. In the presence of pyridine, the intermediates $Mo_2(OPr^i)_6(py)_2(HCCH)$ and $Mo_2(ONe)_6(py)(C_4H_4)$ have been isolated, structurally characterized and shown to be active alkyne polymerization catalysts (148).

7. CONCLUDING REMARKS

The chemistry of metal-metal bonded compounds is approaching its adolescence. Our understanding of the structure and bonding in these compounds is rapidly approaching the point that new discoveries will routinely be incorporated into or merely modify existing theories. Certainly a failure to acknowledge the existence of metal-to-metal quadruple bonds in hundreds of Mo_2^{4+} containing compounds could be likened to holding a belief in a "flat earth". The evidence for multiple bonds between metal atoms, though gathered within the last 15 years, is overwhelming, being based on structural parameters, a wide variety of spectroscopic techniques, theoretical and computational techniques and above all, internal consistency of all of the data. By contract, we know very little about the reactions of compounds containing metal-metal bonds. For example, simple addition reactions to metal-metal quadruple bonds may lead to triple, double or single M-M bonded compounds or may give complete cleavage, depending upon the substrate, the metal and the ligands. It is fair to say that these changes in metal-metal bonding may be rationalized with 20:20 hindsight, but in not one instance were they

predicted. Similarly, who could have expected that $1,2-Mo_2Br_2(CH_2SiMe_3)_4$ would react with $HNMe_2$ and $LiNMe_2$ to give 1,2- and $1,1-Mo_2(NMe_2)-(CH_2SiMe_3)_4$ compounds, respectively, and furthermore, that once formed, these isomers would not isomerize readily? The point which must be accepted is that we know very little about even the simplest of reactions at polynuclear metal centers. Detailed mechanistic studies are much needed. Currently, while some proclaim the prospects for catalysis by polynuclear and cluster compounds, others argue that clusters are too fragile and note that as yet no cluster catalysis has been demonstrated that a mononuclear compound cannot do equally well or better. Scientifically, these merely represent opinions. In the area of technological applications, we do not yet deserve "cluster catalysis". The move from mononuclear to dinuclear and polynuclear coordination chemistry represents a natural evolutionary process in coordination chemistry and technological applications will surely follow. A detailed understanding of the reactions of metal-metal bonds will be central to this development.

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